# Synthesis, Solution Properties and NMR Spectroscopy of some Polybetaines

by

Mir Mukarram Ali

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

**MASTER OF SCIENCE**

In

**CHEMISTRY**

December, 1998

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**DECEMBER 1998**

# KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN 31261, SAUDI ARABIA

## DEANSHIP OF GRADUATE STUDIES

This thesis, written by **Mir Mukkaram Ali** under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of

**MASTER OF SCIENCE in Chemistry.**

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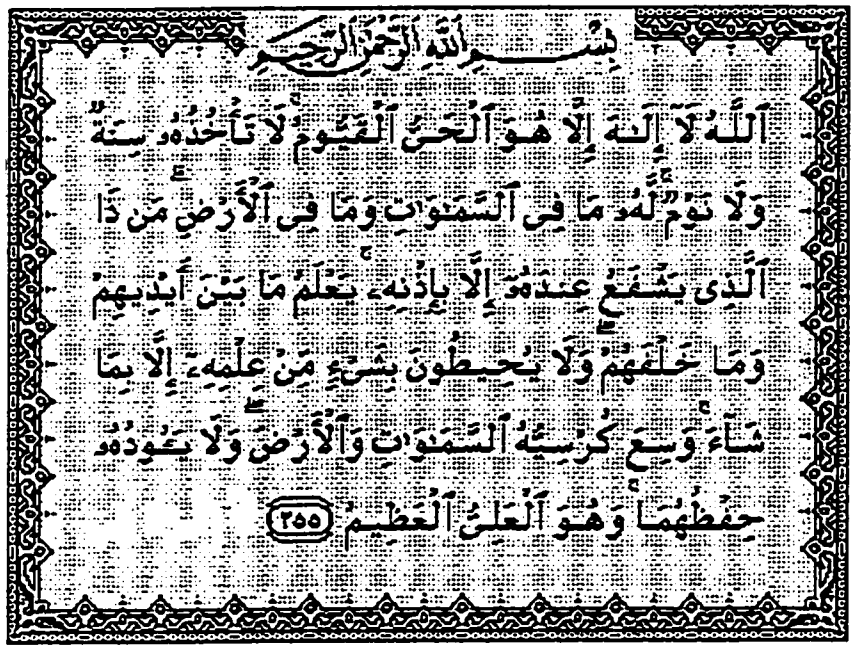
Dr. Shaikh Asrof Ali (Member)

Dr. Mohammad Wazeer (Member)

Dr. Assad A. Al-Thukair
(Department Chairman)

Dr. Abdullah M. Al-Shehri
(Dean of Graduate Studies)

8/5/99
Date


بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ
اللَّهُ لَا إِلَٰهَ إِلَّا هُوَ الْحَيُّ الْقَيُّومُ لَا تَأْخُذُهُ سِنَةٌ
وَلَا نَوْمٌ لَّهُ مَا فِي السَّمَاوَاتِ وَمَا فِي الْأَرْضِ مَن ذَا
الَّذِي يَشْفَعُ عِندَهُ إِلَّا بِإِذْنِهِ يَعْلَمُ مَا بَيْنَ أَيْدِيهِمْ
وَمَا خَلْفَهُمْ وَلَا يُحِيطُونَ بِشَيْءٍ مِّنْ عِلْمِهِ إِلَّا بِمَا
شَاءَ وَسِعَ كُرْسِيُّهُ السَّمَاوَاتِ وَالْأَرْضَ وَلَا يَئُودُهُ
حِفْظُهُمَا وَهُوَ الْعَلِيُّ الْعَظِيمُ ﴿٢٥٥﴾

*Allâh! Lâ ilâha illa Huwa (none has the right to be worshipped but He), the Ever Living, the One Who sustains and protects all that exists. Neither slumber, nor sleep overtake Him. To Him belongs whatever is in the heavens and whatever is on earth. Who is he that can intercede with Him except with His Permission? He knows what happens to them (His creatures) in this world, and what will happen to them in the Hereafter . And they will never compass anything of His Knowledge except that which He wills. His Kursî[II] extends over the heavens and the earth, and He feels no fatigue in guarding and preserving them. And He is the Most High, the Most Great. [This Verse 2:255 is called Ayat-ul-Kursî.]*

*Dedicated to my parents, sister and brother*

# ACKNOWLEDGEMENTS

It gives me great pleasure to acknowledge the dedicated efforts of my Thesis Committee Chairman, Dr. Herman Perzanowski and Dr. Shaikh Asrof Ali. Their enthusiastic participation, guidance and encouragement have been critical to the success of this work. I also want to thank Dr. Mohammad Wazeer for his valuable comments and suggestions.

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# THESIS ABSTRACT

**NAME:** MIR MUKKARAM ALI

**TITLE:** SYNTHESIS, SOLUTION PROPERTIES AND NMR SPECTROSCOPY OF SOME POLYBETAINES

**MAJOR:** CHEMISTRY

**DATE:** DECEMBER, 1998

The quaternary ammonium salt *N,N*-diallyl-*N*-(ethoxycarbonyl)methyl-*N*-(methoxycarbonyl)pentyl ammonium chloride on cyclopolymerization in aqueous medium using t-butyl hydroperoxide as free radical initiator gave the corresponding homopolymer. The copolymer of this quaternary ammonium monomer with sulfur dioxide was prepared in DMSO using ammonium persulfate as the initiator. The homopolymer and copolymer were converted to polybetaines by acidic hydrolysis of ester functionality present on the repeat unit. These polybetaines represent a new class of polymers since they possess a zwitterionic moiety as well as a free electrolytic ion pair on each repeat unit. They possess structural features common to polyampholytes and conventional polyelectrolytes. It is therefore of interest to determine what effect this special structural feature would have on their solubility and solution properties.

A zwitterionic monomer 3-(*N,N*-diallyl-*N*-methoxycarbonyl pentyl) ammoniopropanesulfonate was prepared and its free radical polymerization in aqueous medium using t-butyl hydroperoxide as the initiator gave a conventional polybetaine. A preliminary investigation of its solubility behavior suggested that this polybetaine possesses polyampholytic properties. $^{1}H$, $^{13}C$. DEPT, COSY and CHSHF NMR techniques were used extensively to elucidate the structures of these new monomers and polymers.

**MASTER OF SCIENCE DEGREE**

**KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS**
**Dhahran, Saudi Arabia**

**December 1998**

# ملخص الرسالة

الإسم : مير مكرم علي

عنوان الرسالة : تحضير و دراسة خواص المحلول و مطيافية الرنين النووي المغناطيسي (NMR) لبعض مبلمرات البولي بيتاينات

التخصص : كيمياء

التاريخ : ديسمبر ١٩٩٨

تم في هذا البحث دراسة البلمرة الحلقية لملح الأمين الرباعي N,N - ثنائي ألايل -N- (إيثوكسي كاربونيل) - ميثايل -N- (ميثوكسي كاربونيل) بتايل أمونيوم كلوريد في وسط مائي باستخدام ثـــالثي- بيوتـــايل هيدروبيروكسيد كحذر حر بادئ للتفاعل حيث ينتج المبلمر المتجانس المطلوب ، ويتم تحضير المبلمر المشترك من مونومر الأمين الرباعي السابق مع ثاني أكسيد الكبريت في وجود مركب ثنائي ميثايل أكسيد الكـــبريت (DMSO ) كمذيب ، ومركب فوق كبريتات الأمونيوم كبادئ للتفاعل ، ويتم تحويل المبلمر المتجـــانس و المبلمر المشترك إلى بولي بيتاينات بواسطة التميه الحامضي لمجموعة الإستر الوظيفية في الوحدة المتكررة .

تمثل البولي بيتاينات تصنيف جديد في علم المبلمرات حيث تحتوي على جزء ثنائي الشـــحنة (Zwitterion)- (شحنة سالبة و شحنة موجبة) كما هو الحال في زوجي الأيونات الحرة الإلكتروليتية الموجودة في كل وحـدة تكرار ، كما تحتوي على صفات شكلية بنائية مشتركة مع المبلمرات ذات المجموعات المحبة والكارهة للمـــاء (Polyampholyte) ومبلمرات البولي إلكتروليت التقليدية ، لذلك كان من المهم معرفة و تحديد ماهيـــة تأثير هذه الصفات الشكلية البنائية خاصة على ذائبية هذه المبلمرات وخواصها في المحاليل.

من جهة أخرى تم تحضير مونومر ثنائي الشحنة وهو ٣-(N,N ثنائي ألايل-N-ميثوكسي كاربونيل بتايل ) أمونيوبروبان سلفونيت ، وتم تحويله إلى مبلمر بطريقة بلمرة الجذر الحر في وسط مائي باستخدام ثـــالثي - بيوتايل هيدروبيروكسيد كبادئ للتفاعل لينتج لدينا البولي بيتاين التقليدي . نتائج البحث التمهيدية لذائبيـــة هذا المبلمر قررت احتوائه على خواص البولي أمفوليت (Polyampholyte) وقد استخدمت تقنيات مطيافية الرنين النووي المغناطيسي بشكل واسع لتحديد التركيب البنائي لكل من هذه المونومرات والمبلمرات الحديثة ، وهذه التقنيات هي: مطيافية الهيدروجين $^{1}H$ ، مطيافية الكربون النظير $^{13}C$ ، مطيافية الزيادة الغير مشـــوهة بواسطة الإستقطاب الإنتقالي DEPT، مطيافية الإرتباط COSY ، وأخيرا مطيافيـــة الإرتبـــاط لإزاحـــة الكربون و الهيدروجين CHSHF .

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران ، المملكة العربية السعودية

ديسمبر ١٩٩٨

# CHAPTER 1

# INTRODUCTION

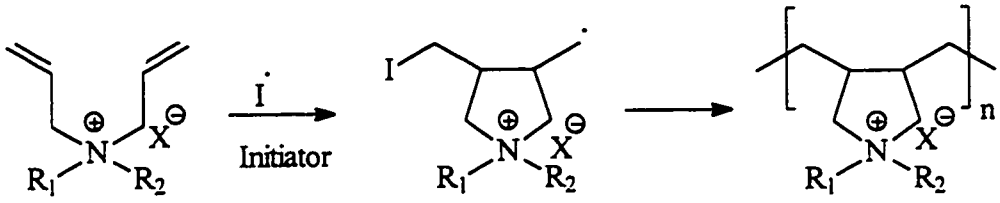
## 1.1 Introduction

Water soluble polymers are produced in large quantities and are widely used in industry and consumer products. All water soluble polymers share the common element of having hydrophilic polar functional groups that may be non-ionic, anionic or cationic. The anionic and cationic polymers together are referred to as polyelectrolytes, while the non-ionic ones are called non-polyelectrolyes.

Cationic polyelectrolytes can be grouped into three categories: ammonium (primary, secondary, tertiary and quaternary); sulfonium; and phosphonium compounds. Of these the ammonium based polymers are the most extensively used in industry.[1-3] Phosphonium compounds have not been synthesized to high molecular weights, and sulfonium monomers are generally unstable and less readily available than quaternary ammonium monomers.[4] The quaternary ammonium functional group is highly hydrophilic lending high water solubility to quaternary ammonium polyelectrolytes. The polymers have been used extensively in water treatment, as flocculating agents,[5] in sludge

dewatering,[5,6] in sedimentation of suspended polymers,[7,8] in enhanced oil recovery,[9] and for electroconductivity in electropolarography.[10,11]

A large number of diallylquaternary ammonium salts have been polymerized by Butler and coworkers to yield linear water soluble polymers with little or no residual unsaturation.[12-15] Diallyl quaternary ammonium salts **1** are 1,6 – dienes that polymerize via an intra-inter molecular chain propagation (termed cyclopolymerisation) through the 5-membered cyclic structure **2** to yield linear water soluble polymers **3** (scheme 1).




**1** **2** **3**

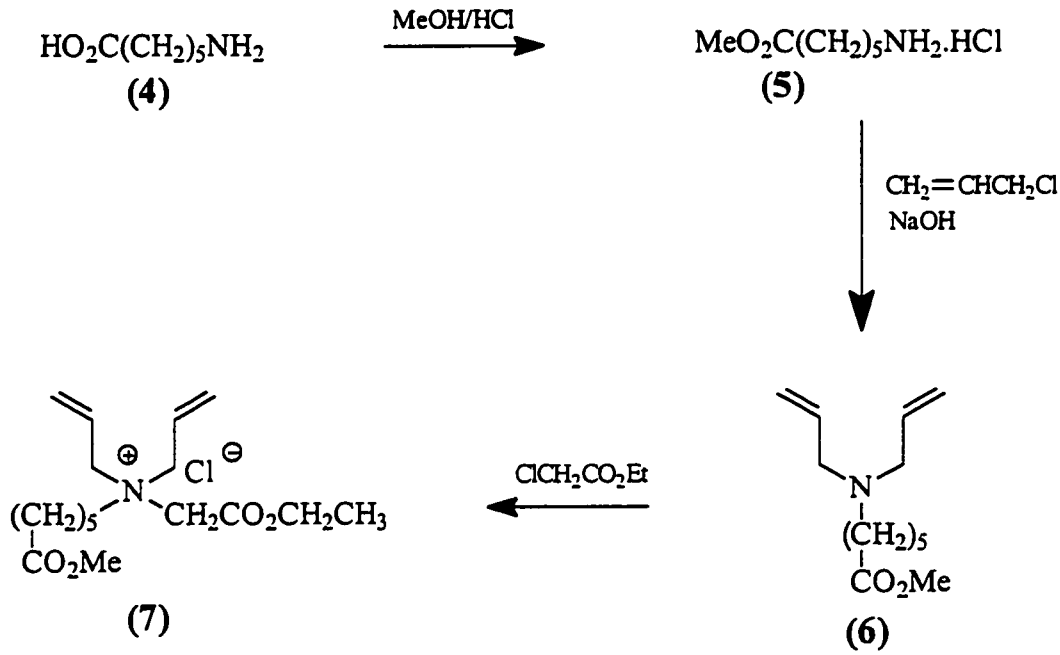
**Scheme 1**

Diallyl quaternary ammonium salts are copolymerised with $SO_2$ on a commercial scale and the resulting polysulfones have various industrial uses.[16] Crosslinked polysulfones are used as ion-exchange beds. Tri- or tetra-allyl ammonium salts have been used in removal of salinity from brackish water[17] and in the extraction of uranium.[18]

Copolymerisation of salts **1** with monomers containing some hydrophobic moiety yield copolymers, which undergo hydrophobic association in aqueous solution. This property is of interest in applications where the viscosification of water is desired such as in enhanced oil recovery processes.[19]

## 1.2 Aim of the work

The objective of this research is to synthesize monomer **7** from the widely available starting material 6-amino-caproic acid **4** as shown in scheme 2.

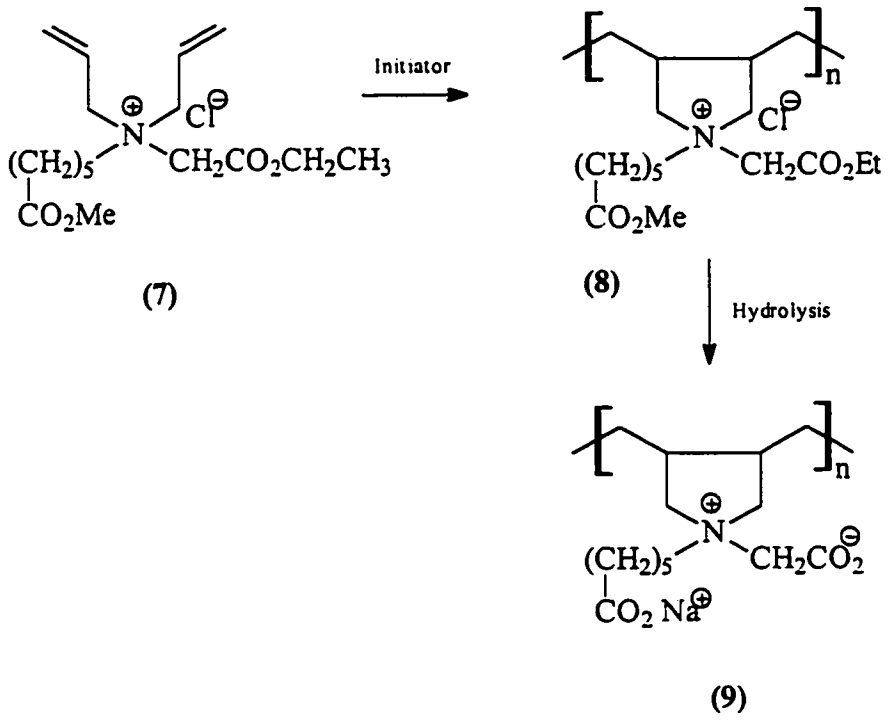



**Scheme 2**

The monomer **7** would then be polymerized to yield the homopolymer **8**. The polymerization reaction conditions will be optimized to obtain high molecular weight polymers in good yield. The most suitable free radical initiator, solvent, reaction temperature and time will be determined.

Polymer **8** will be hydrolyzed to yield the zwitterionic polymer **9** by acid hydrolysis

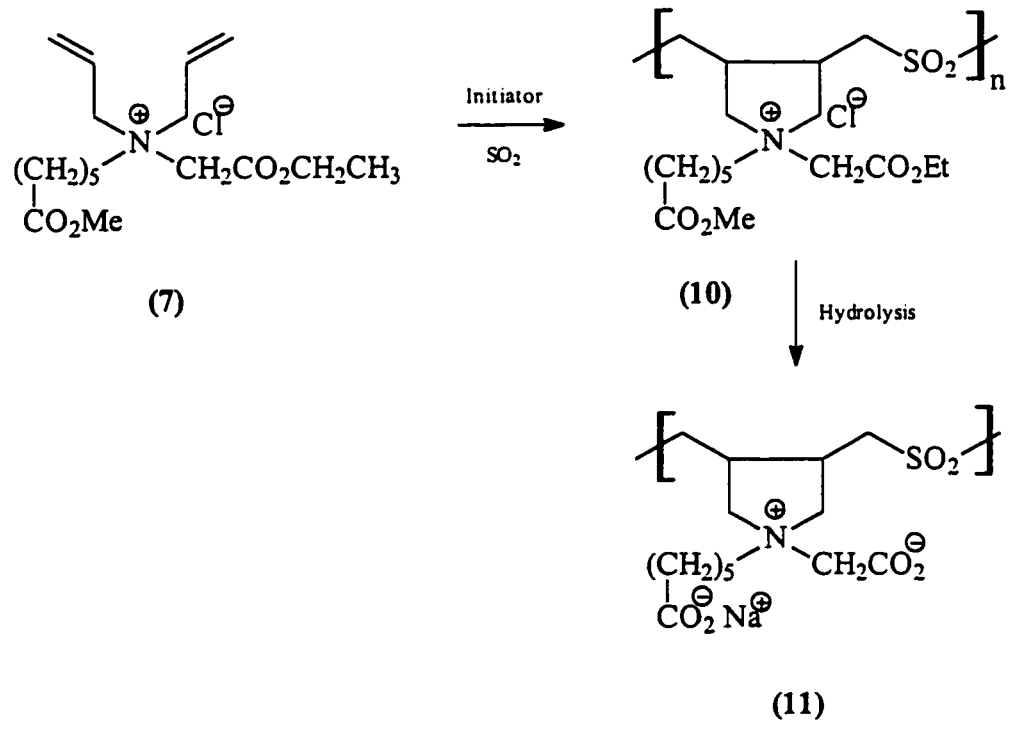
(Scheme 3). The rheological properties of **8** and **9** will be studied.




**Scheme 3**

The copolymerization of monomer **7** with $SO_2$ and hydrolysis of the copolymer **10** to the zwitterionic polysulfone **11** (Scheme 4) will be investigated.

The copolymerisation reaction conditions will be optimized and rheological studies of the copolymers **10** and **11** will be conducted.



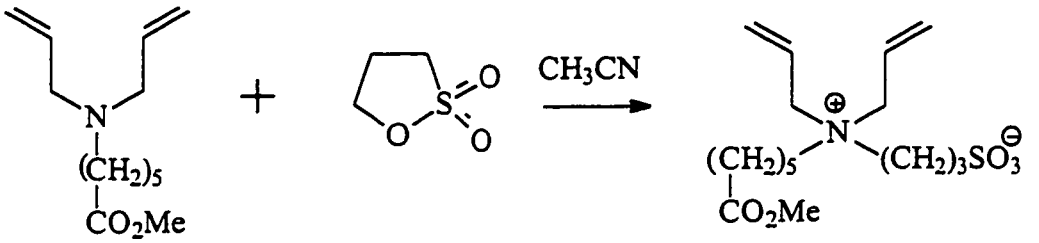

**Scheme 4**

This research intends to determine the rheological behavior of zwitterionic polymers **9** and **11**. The structure of these polymers incorporates an electrolytic ion pair as well as a zwitterionic moiety. It would be interesting to investigate the solubility of these polymers in aqueous medium. Zwitterionic polymers (known as polybetaines) are insoluble in water and can be solubilised by addition of strong electrolytes such as sodium chloride. This is because the added electrolyte ions break the strong interchain associations occurring in polybetaines. It will be determined whether the presence of electrolytic ion pair in zwitterionic polymers **9** and **11** will impart water solubility in the absence of added electrolyte.

Further more, polybetaines exhibit increasing intrinsic viscosity in solutions of higher salt concentrations. This is referred to as antipolyelectrolyte effect.[20] Polyelectrolytes, as is well known, exhibit decreasing intrinsic viscosity with increasing salt concentration.

Given the fact that the structures of polymers **9** and **11** incorporate features present in conventional polyelectrolytes and also polybetaines, it is desired that their solubility and viscosity behavior in presence of added salt (NaCl) be determined.

It is also our aim to synthesize monomer **12** from precursor **6** as shown in scheme 4.




**(6)** **(12)**

**Scheme 5**

Monomer **12** differs from monomer **8** in that it does not possess the relatively acidic protons on the carbon between the anion stabilizing positive nitrogen and carbonyl group. It is therefore expected that its polymerization would proceed with better yield.

# CHAPTER 2

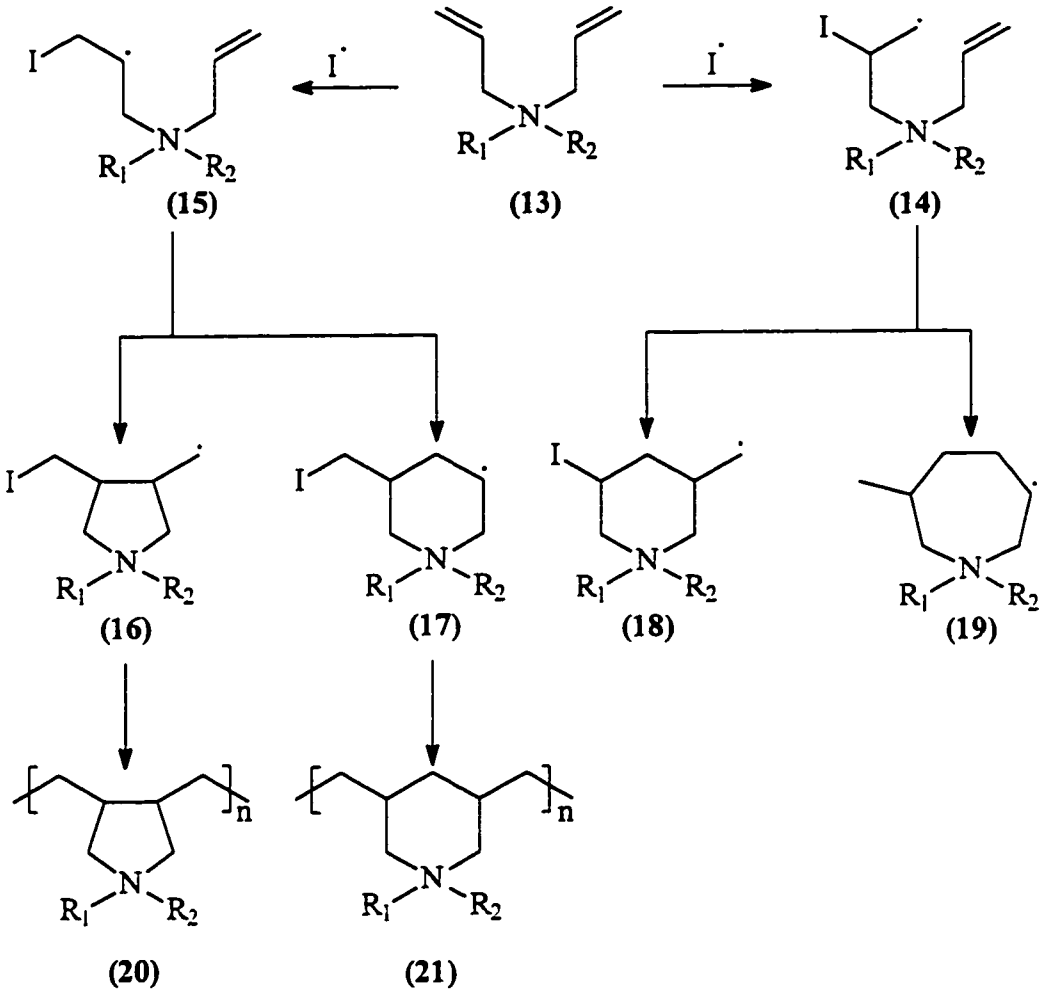
# HISTORICAL DEVELOPMENT

## 2.1 History of polymerization of diallyl amines

Diallyl amines belong to the broad class of non-conjugated dienes. In the early 1930's Staudinger[21] proposed that non-conjugated dienes lead to crosslinked, hence insoluble, non-linear polymers or copolymers. In 1949, Butler and Bunch [11] polymerized tri- and tetra-allyl quaternary ammonium salts to form highly crosslinked water insoluble polymers. The first instance of an exception to Staudinger's proposal was reported in 1951, when Butler and Ingley[22] polymerized diallyl quaternary bromide salts to yield water-soluble linear polymers. Early investigation involving degradation studies[23] revealed that the polymer possesses cyclic structures. Flory[24] proposed a six-membered structure for radical initiated cyclopolymerization of 1,6–dienes (symmetrical or unsymmetrical) where predominance of more stable intervening radicals controls vinyl polymerization.

Scheme 6 shows the possible ring structures in cyclopolymerization of diallyl amines. It has now been shown that the cyclopolymerization of diallyl quaternary ammonium salts leads to five-membered cyclic structure **20** *via* the less stable intermediate **16** under

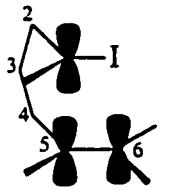
conditions of kinetic control[25]. The formation of this structure by the reaction sequence **13 → 15 → 16 → 20** corresponds to a head-to-head polymerization process.




**Scheme 6**

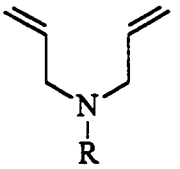
Most non-conjugated dienes appear to undergo cyclopolymerization involving an intramolecular ring-closing mechanism rather than polymerization through a single allyl group which would lead to crosslinked polymer[2]. The preference for cyclisation has been attributed to a smaller decrease in entropy relative to intermolecular addition. The kinetic control of the intramolecular cyclisation reaction is explained in terms of stereoelectronic

requirements of the transition state[26]. Maximum overlap of the half-filled p-orbital with the vacant π* orbital of the double bond demands the approach of the radical along a vertical line from one of the carbon atoms of the double bond with the orbitals holding the three electrons in the same plane throughout the reaction. This requirement is met in the 1, 5 cyclisation but not in the 1, 6 cyclisation.




However, introducing bulky 5 substituents leads to increasing preference for the six-membered ring structure.

Diallyl amines do not undergo free radical polymerization readily, the protonated or quaternary salts do polymerize. The presence of electrophilic N-substituents in diallyl amines **22** activates the monomers towards radical attack.[27]

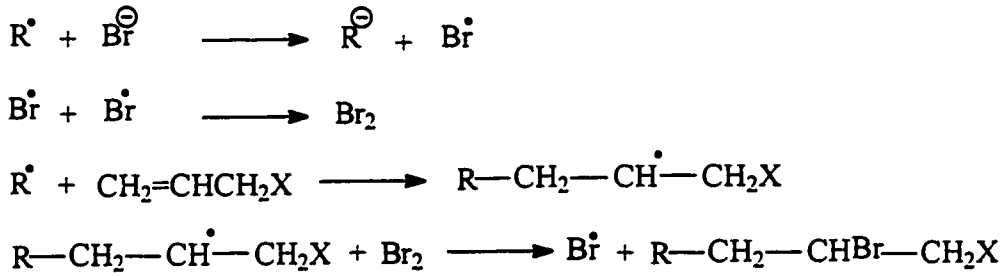



(R= CN, COR', $SO_2R'$ etc.)

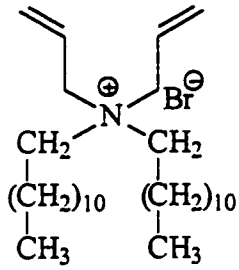
**22**

Polymers of diallyl quaternary ammonium chlorides have higher molecular weights (and are therefore more useful) than the polymers of diallyl quaternary ammonium bromides.[28] Initiator radicals probably oxidize the bromide ion more easily to bromine, which then

inhibits polymerization by consumption of initiator radicals, and by termination of propagating chains.



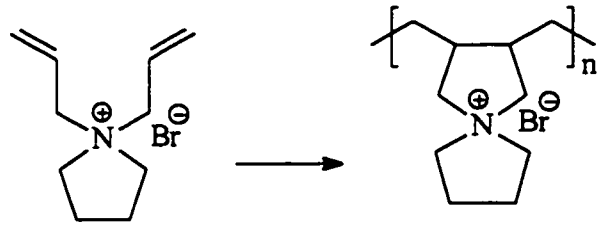
Diallyl quaternary ammonium bromide **23** is a vesicle forming monomer.



**(23)**

The double-tail lipophylic portion of **23** makes it capable of forming vesicles in water. Polymerization of **23** by gamma ray irradiation yields the polymeric counterpart. It has been shown that the polymerized vesicles retain the structure of the monomeric vesicles and simultaneously exhibit higher stability.[29]

*N,N*-Diallyl pyrrollidinium bromide (DAPB) **24** has been polymerized to poly-DAPB **25** by free radical polymerization.

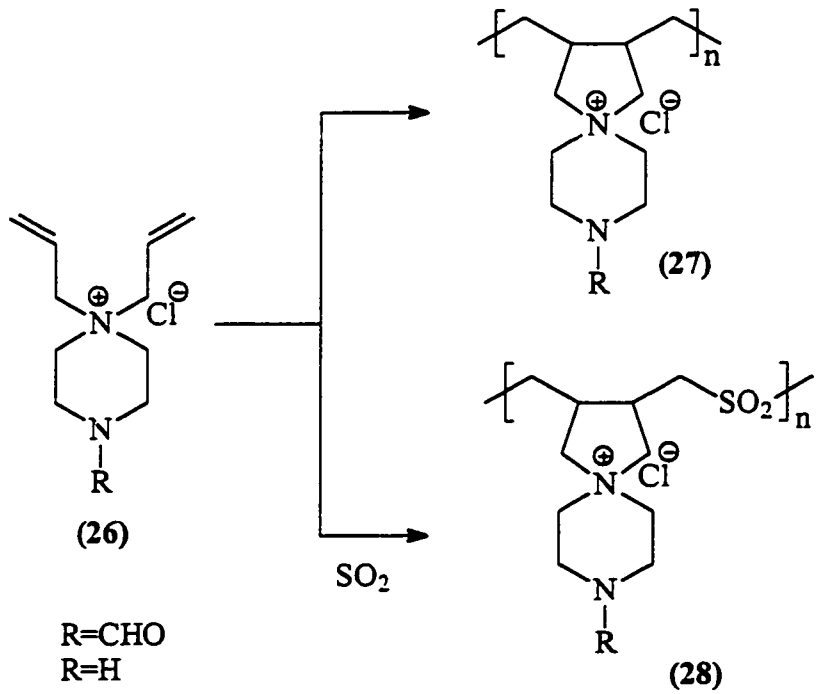


DAPB
(24)

Poly DAPB
(25)

That the polymerization proceeds by cyclopolymerisation leading to the five-membered ring structure was confirmed by comparison of $^{13}C$ NMR spectra of poly-DAPB with those of model compounds.[30]

*N,N*-Diallyl-4-formylpiperazinium chloride **26** was polymerized using tertiary butyl hydroperoxide initiator. The aqueous two-phase system of the homopolymer **27** and copolymer (with $SO_2$) **28** was studied.[31]



(26)

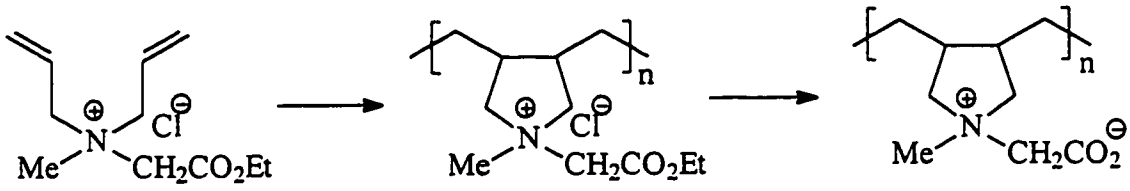
R=CHO
R=H

$SO_2$

(27)

(28)

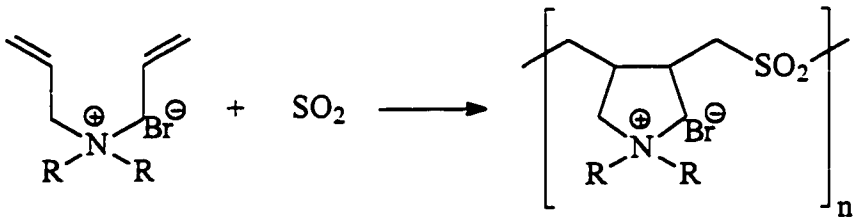
Polymerization of **29** using ammonium persulfate (APS) initiator to polyelectrolyte **30** which was hydrolyzed to the zwitterionic polymer **31** has been reported recently[32]. It has been shown that **31** exhibits antipolyelectrolyte viscosity behavior like most zwitterionic polymers.




**(29)** **(30)** **(31)**

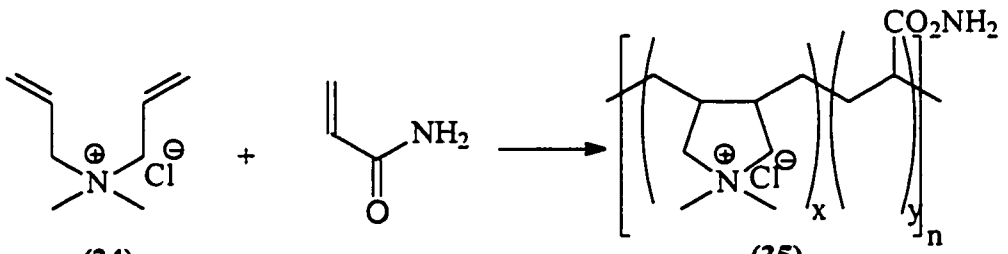
## 2.2 Copolymerization in non-conjugated dienes

Alternating copolymers **33** are obtained on cyclopolymerization of diallyl compounds **32** with sulfur dioxide[33,16] in different solvents with free radical initiators as ammonium persulfate, azobisisobutyronitrile, t-butylhydroperoxide, dilauroyl peroxide.



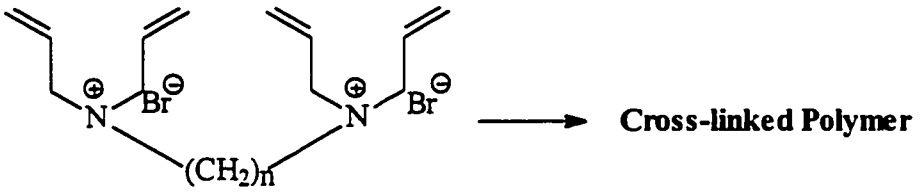

**(32)** **(33)**

It is reported[34] that dimethyldiallylammonium chloride **34** undergoes copolymerization with acrylamide to give the polymer **35**.




(34) (35)

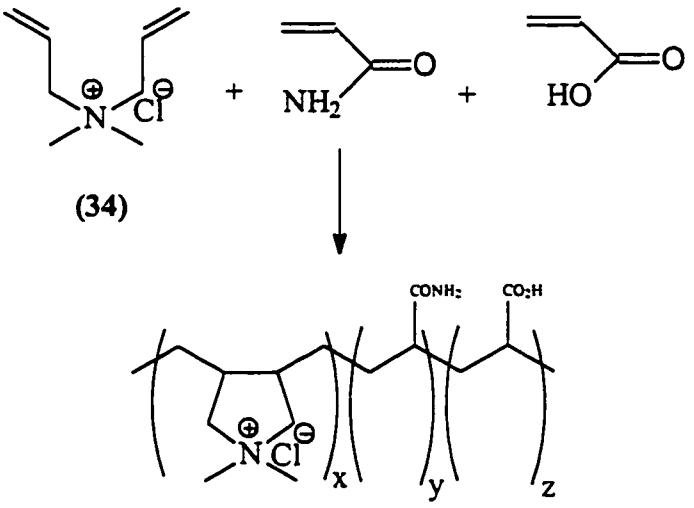
Ion-exchange resins were obtained by the polymerization of the tetraallyl derivatives **36** of 1,n-diaminoalkanes[35-37].




(36)

Amphiphilic cyclopolymerization[38] of diallydimethylammonium chloride and diallylalkyloxybenzylmethylammonium chloride was studied by free radical polymerization in aqueous solution. It was observed that addition of sodium dodecyl sulfate (SDS), below the critical micelle concentration, to the copolymer solution results in a large increase in the viscosity of the polyelectrolyte.

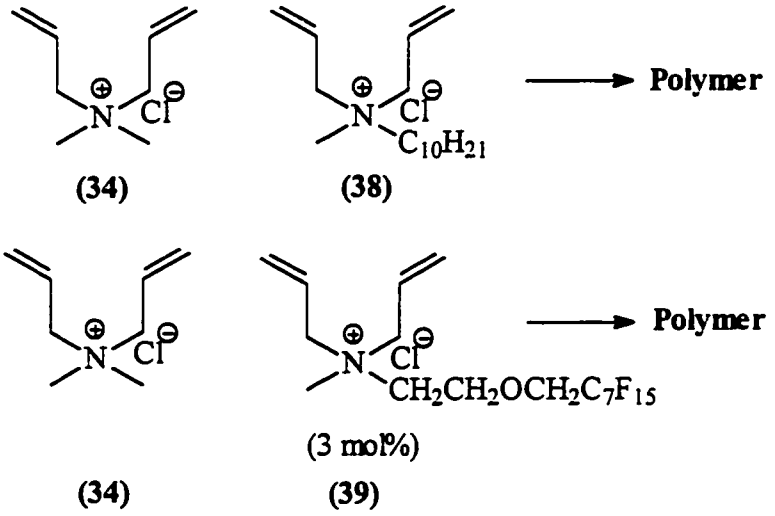
Polyelectrolytes have also been synthesized by terpolymerizing dimethyldiallylammonium chloride with acrylamide and acrylic acid[39]. These polymers **37** are used as dry strength resins in paper.[40]




(34)

(37)

Hydrophobically associating ionic copolymers[19,41,42] of diallyldimethylammonium chloride **34** with 1 to 4 mol% of diallyl decylmethylammonium chloride **38** and methyldiallyl-(1,1-dihydropentadecafluorooctaoxyethyl)-ammonium chloride **39** are synthesized and the copolymer showed significant increases in the viscosity compared to poly(diallyldimethylammonium chloride).




(34) (38)

(34) (39)

A review and use analysis of poly(dialkyldiallylammonium halides) has been published.[3] A variety of commercial products have been developed using cyclopolymerization of these quaternary salts. Poly(dimethyldiallylammonium chloride) is the first polymer in this series to be manufactured by a number of suppliers. It possesses optimum functional properties for application to electrographic paper reproduction processes.[1] This polymer has also found application as paper additives. It is used in water treatment as a flocculent. In the industry this polymer has found application as a coagulant in the coal floatation process, in foam floatation of metal sulfides, and in the tin, zinc and lead electroplating industries. In the cosmetic field it is used as a de-emulsifier of dispersed oils, as a biocide in water, and as a detergent additive.

The copolymers of these quaternary salts with sulfur dioxide[16] have similar industrial uses. Tetraallyl diammonium dichloride salts give ion-exchangers of both superior rate and capacity for use in extraction of uranium.[18] Polytriallylamine[43] is reported to be a thermally regenerated ion exchange resin[17] for the cheap removal of salinity from brackish waters. Diallylamine hydrochloride with a suitable crosslinker is reported to give a polymer used as a super anion exchanger. Cyclopolymerization of suitable salts have also resulted in the formation of strongly basic ion exchange resins.[35,37] The hydrophobically associating copolymers may have potential application in enhanced oil recovery and other applications where viscosification of water is of interest.

Polyelectrolytes are generally prepared by free radical (homo- and co-) polymerization of an ionic monomer or neutral monomer. In the latter case the subsequent reaction on the preformed neutral polymer leads to ionic polymers. However the first case offers greater advantage in controlling over the structure and properties of the final polyelectrolyte. The

second case is more difficult to control as the amount of charge becomes greater and greater during conversion of a neutral polymer to one of high charge density and as such most reactions rarely go to completion.

There has been considerable academic and industrial interest in the preparations of new ionic polymers.[44,6] These studies included the areas of cationic and anionic polyelectrolytes, since both classes have unique chemical and physical properties.

## 2.3 Polyampholytes

Ampholytic (zwitterionic) polymers are either formed from polymerization of inner salt (zwitterionic) monomer or from the preformed neutral polymer.

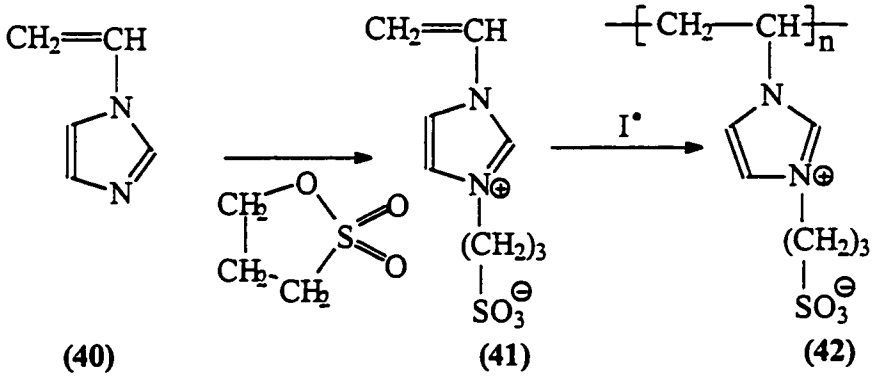
The polyampholytes show unusual properties in aqueous solution[45,46]. The polymers are insoluble in water and have hydrogel characteristics. However, the polymers could be dissolved in certain aqueous salt solutions. The solution properties are found to depend on the type and concentration of the salt added. In contrast to polyelectrolytes, the reduced viscosities of polyampholytes increases with increased salt concentration. The greater the site binding ability of either the cation or anion, the greater the reduced viscosity.[46]

For the solubilization of polyampholytes by aqueous salt solution, the cations and anions of low molecular weight electrolytes could be considered to enter ionically crosslinked network of the polymer thorough osmotic forces.[47] These forces cause the polymer to

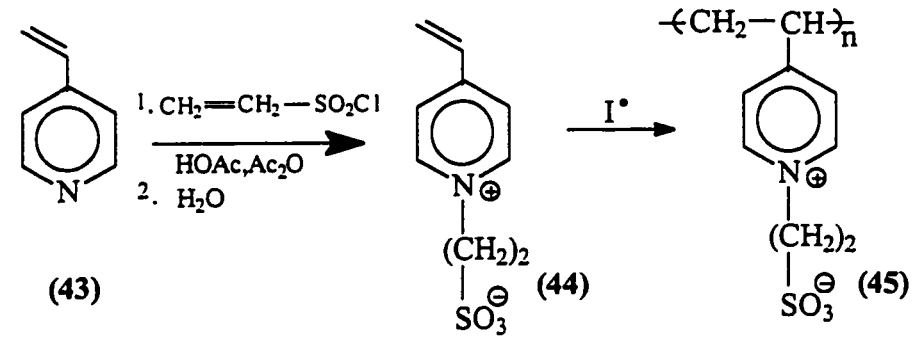
swell when placed in water. The insolubility of polyampholytes in water is attributed to the fact that the osmotic forces that tend to draw solvent into the polymer are not sufficient to rupture the ionic crosslinks. Polyampholyte swells until elastic forces of the network balance the osmotic forces. In the presence of added salt (NaCl) the solvent ($H_2O$) along with the mobile ions is drawn into the polymer, and the polymer swells as usual. However the mobile ions of the added salt neutralizes a portion of the ionic crosslinks resulting in the continual decrease of the elastic forces which tend to oppose the continued swelling. As a result the polymer swells until the gel finally dissolves.

One of the major drawbacks of the use of high molecular weight polyelectrolytes in enhanced oil recovery (EOR) is the drastic decrease of the viscosity of their aqueous solutions in presence of salt (NaCl etc).[48] However zwitterionic polymers show "antipolyelectrolyte behaviour"[49] and have low or no solubility in water but greatly enhanced solubility and extensive chain expansion, hence viscosification, upon increasing salt concentration.

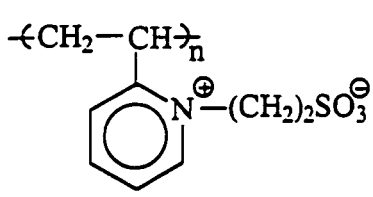
Quaternarization of 2-vinylimidazole **40** with propane sultone gives inner salt **41** which on free radical polymerization yielded the polyampholytic homopolymer **42**.[47]



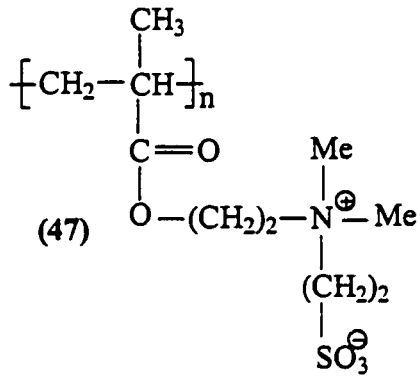
A disadvantage in all reported synthesis of polyvinylsulphobetains is the use of sultones, which are carcinogenic compounds.[50] Another disadvantage is that only propane- and butane- sultones are known to yield ampholytic monomer. In order to circumvent the problem the following monomer **44** was synthesized using alkenylsulfonylchlorides.[51]



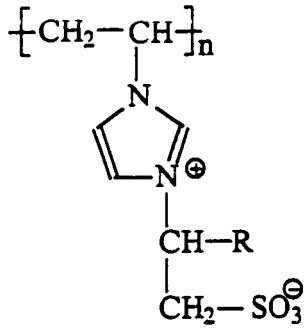

**(43)** **(44)** **(45)**



**(46)**



**(47)**



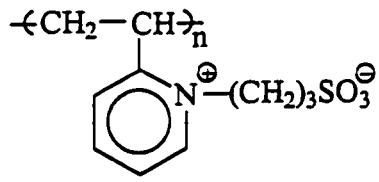
**(48)** R = H

**(49)** R = Me

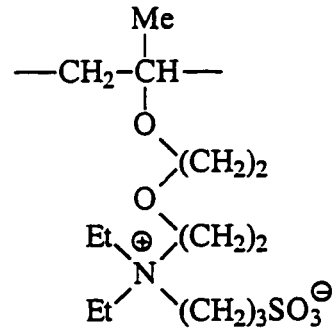
The monomer on free radical polymerization afforded the polyampholyte **45**. Likewise, the polyampholytes **46-49** were synthesized. As anticipated the polyampholytes **45-48** are

insoluble in water but readily dissolves in aqueous solution of NaCl. Such behavior has been interpreted[49,52] by assuming the presence of a collapsed coil in water due to intrasalt and intrachain interactions. Such interactions are broken up in presence of added low molecular weight electrolytes. While the polyampholyte **48** was found to be insoluble, the polymer **49** readily dissolves in water. The presence of bulky groups near the quaternary centre effectively diminishes the effectiveness of the intrasalt and intrachain interactions. Structural modifications thus effect the delicate balance between intramolecular interactions and hydration. The temperature and molecular weight have also been shown to govern the solubility of polyampholyes[49].

As of 1987 only two other polysulphobetains **50** and **51** were known[53] to be soluble in water.



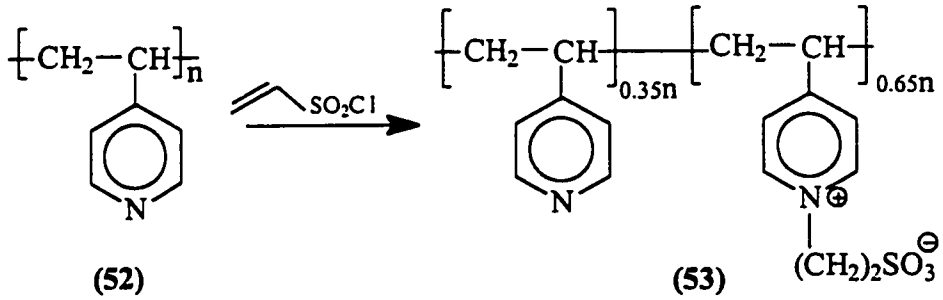
**(50)**



**(51)**

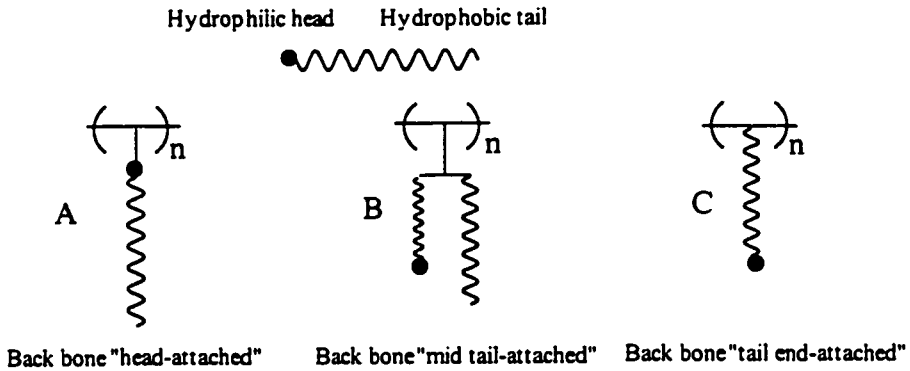
Their solubility was again attributed to the presence of bulky groups near the quaternary nitrogen centre.

Attempts[51] to quaternarize the polymer **52** was accomplished with a yield of only 65%.

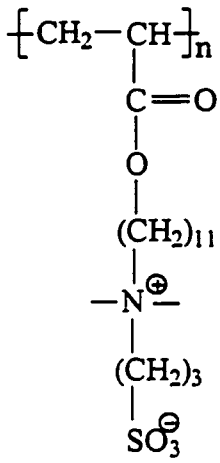



(52) (53)

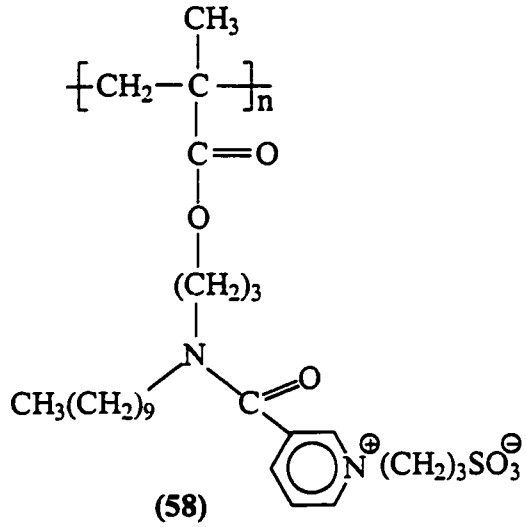
Synthesis and bulk properties of several polyzwitterionic surfactants have been reported.[54,55] The solubility of these polymers is correlated with their molecular geometry. Molecular architecture of polyampholytic surfactants (polysoaps) envisages three main type of structures. In structure **54** the charge centres remain close to the polymeric backbone and is called "head-attached" type. Structure **55** represents polyampholyte of the "mid tail-attached" type. The structure **56** represents polymers of the "tail-end" type where the hydrophobic tail is attached to the backbone. Polymer **57** ("tail end-attached" type) is found to be soluble in formamide and water but insoluble in ethanol. The polymer **58** ("mid tail-attached" type) is soluble in formamide but insoluble in water and ethanol.



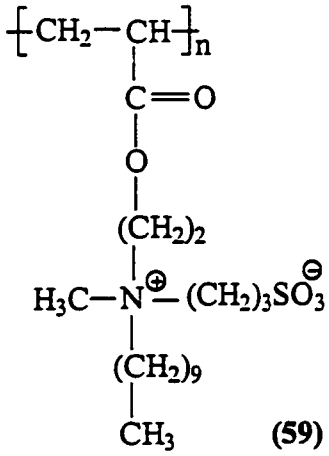

**(54)** **(55)** **(56)**



**(57)**



**(58)**



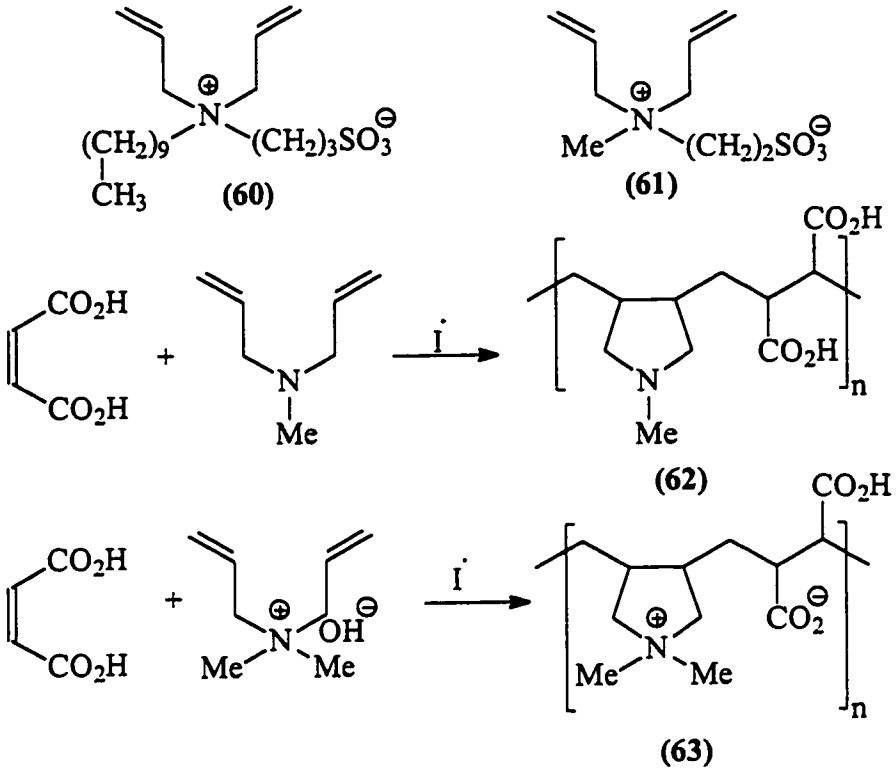
**(59)**

The polymer **59** ("head-attached type") however is found to be insoluble in water and formamide but soluble in ethanol. The tailend attached type polymers as represented by

**57** is found to be soluble in water. It was noted that the solubility of these polymers in water is improved by adding salt as expected.

Obviously, the "skin" of the polymers exposed to the solvent mainly controls the solubility characteristics. Thus ionic / zwitterionic "skins" require polar solvents and hydrocarbon skins require less polar solvents. In agreement with this, polymer **58** which represents the mid-tail attached type exhibits intermediate solubility behavior. These fully zwitterionic polymeric surfactants represent an unconventional but interesting type of micellar polymers (polysoaps). They combine advantageously the behavior of ionic and non-ionic polysoaps.

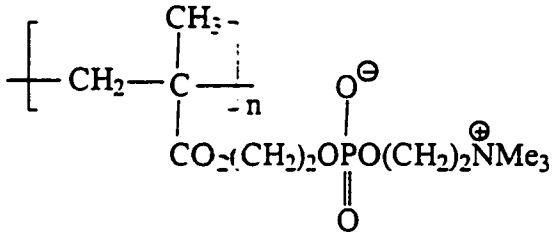
There are only a few references in literature of polyampholytes derived from *N*, *N*-diallyl quaternary ammonium monomers. Zwitterionic polysoaps are prepared by radical homopolymerization of the monomer **60**.



While the homopolymer of the sulfobetaine **61** has been reported in the literature[51], the solution properties of this polyampholyte have not been described.

Alternating ampholytic copolymers of maleic acid with allylamine, diallylamine, methydiallylamine and diallyl quaternary ammonium salt were synthesized by free radical polymerization[56] (to give for example the copolymers **62**, **63** etc.). The copolymers are characterized by viscometry, potentiometry and turbidimetry and their properties are found to depend on pH and ionic strength of the aqueous solutions of the polymers. The influence of the cationic units on solution properties of the polyampholytes is discussed from the aspect of zwitterion formation. It was found that the viscosity of the polymers (e.g. **63**) decreases with increasing concentration of added NaCl, a marked contrast to the behavior observed in case of usual polyampholytes.

Ionic strength (I), pH and dependence of the intrinsic viscosity ([η]) of betaine-type polyampholyte **64** have been investigated recently[57].



**(64)**

The linear relationship between $1/\sqrt{I}$ and [η] for ordinary polyelectrolyte was also observed for the polyampholyte (**64**) at low ionic strength near the isoionic pH (3.35) and over a wide range of ionic strength at other pH. At high ionic strength and at pH 4, a reverse tendency is observed i.e. viscosity increases with increasing ionic strength. This suggests the release of attractive interactions between different charges with the increase of ionic strength. The polyampholyte behaves as a polyelectrolyte when positive charges are excessively populated in the molecule (pH=1.0) and also even when a slight amount of net charges exists in the molecule as long as the magnitude of ionic strength is sufficiently low. Near the isoelectric point, where the net charge in the molecule reduces to zero, the intramolecular attraction between oppositely-charged groups on the chain is expected to make the polyampholyte coil tightly [58,59] in salt free condition and to be expanded with increasing ionic strength. The drag reduction efficiency of several well-characterized water-soluble polyampholytes has been studied[60]. Polyampholytes can reduce the energy loss due to friction in turbulent flow. Polymer molecules interact with vortices that are formed in turbulent flow and dissipate energy necessary for the vortices to grow and thus reduces turbulence.

Polyampholytes have found applications[61] in biosensors and in amphoteric buffer for electrophoresis. Polyampholytes can also serve as a simple model[62-64] for understanding the complex behavior of random copolymer such as proteins. Preparation of novel biodegradable polyampholyte from partially dicarboxylated chitosan has been reported.[65]

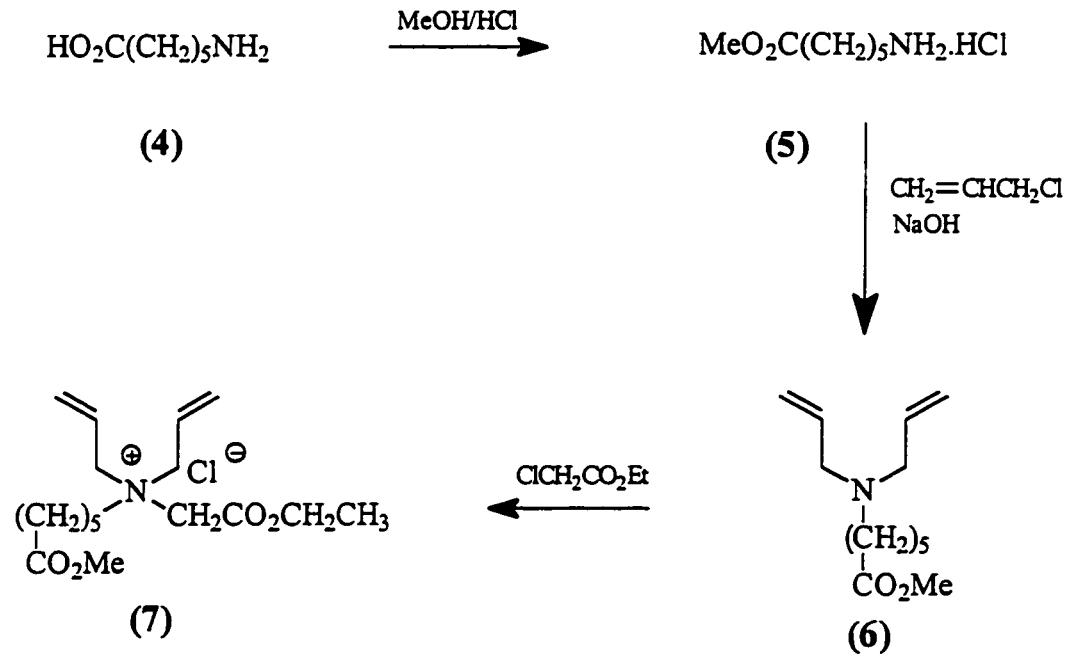
Complexation behavior of proteins with polyampholytes using turbidimetric titration has been investigated.[66] Acrylic polyampholytes have been used for protein separations.[67] Recent[68] study also include the thermodynamic investigation of the sorption of $Fe^{3+}$ and $Cu^{2+}$ ions by a fibrous polyampholyte.

# CHAPTER 3

# RESULTS AND DISCUSSION

## 3.1. Synthesis of Monomer

The cheaply available precursor, 6-aminocaproic acid **(4)** was converted into the corresponding methyl ester **(5)** with simultaneous conversion of the amine functionality into the hydrochloride salt as shown in Scheme 7.




**Scheme 7**

The procedure described by Garmaize[69] was used. The FTIR Spectrum of **(5)** is shown in

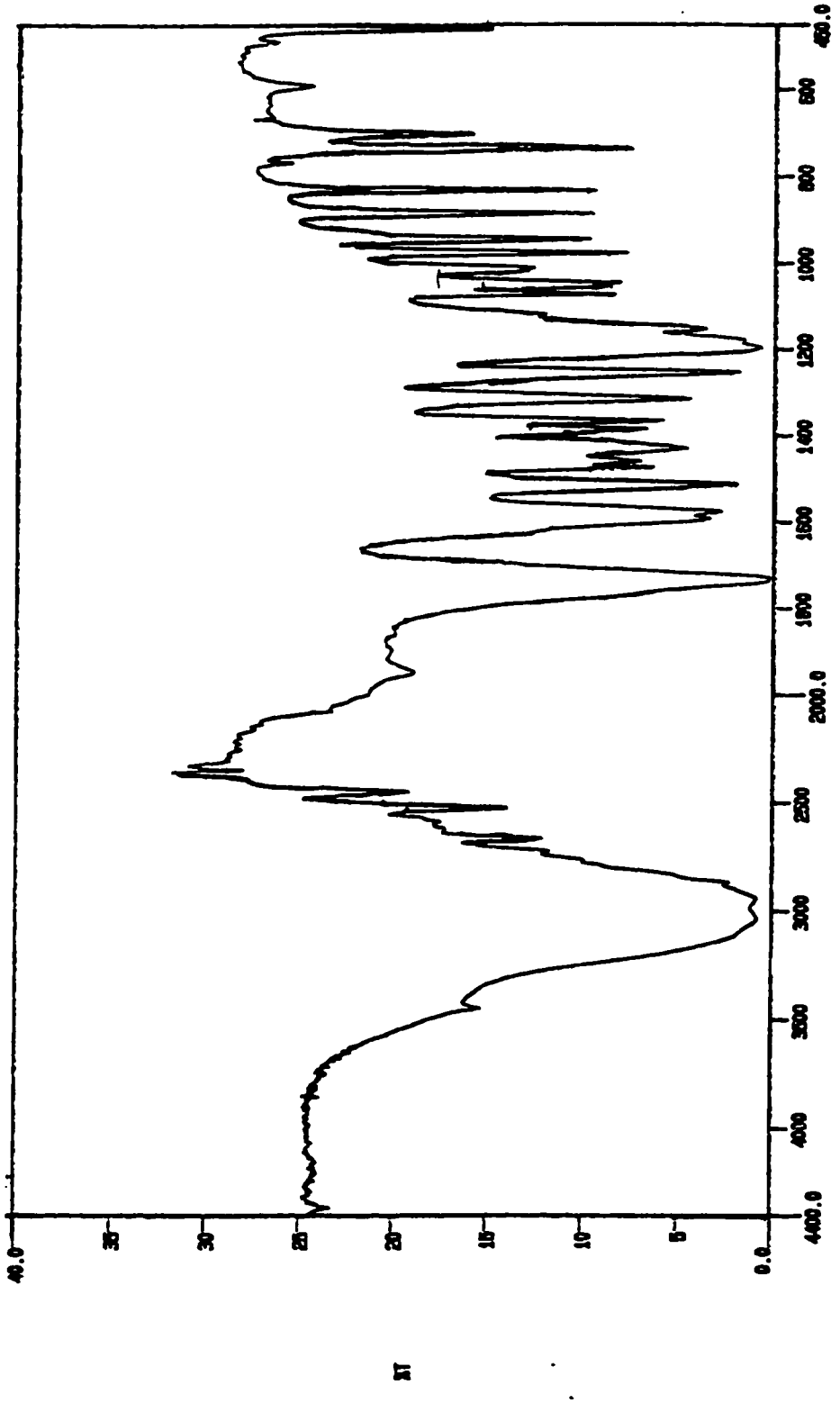



Figure 01 FTIR spectrum of **(5)** in KBr at 20°C

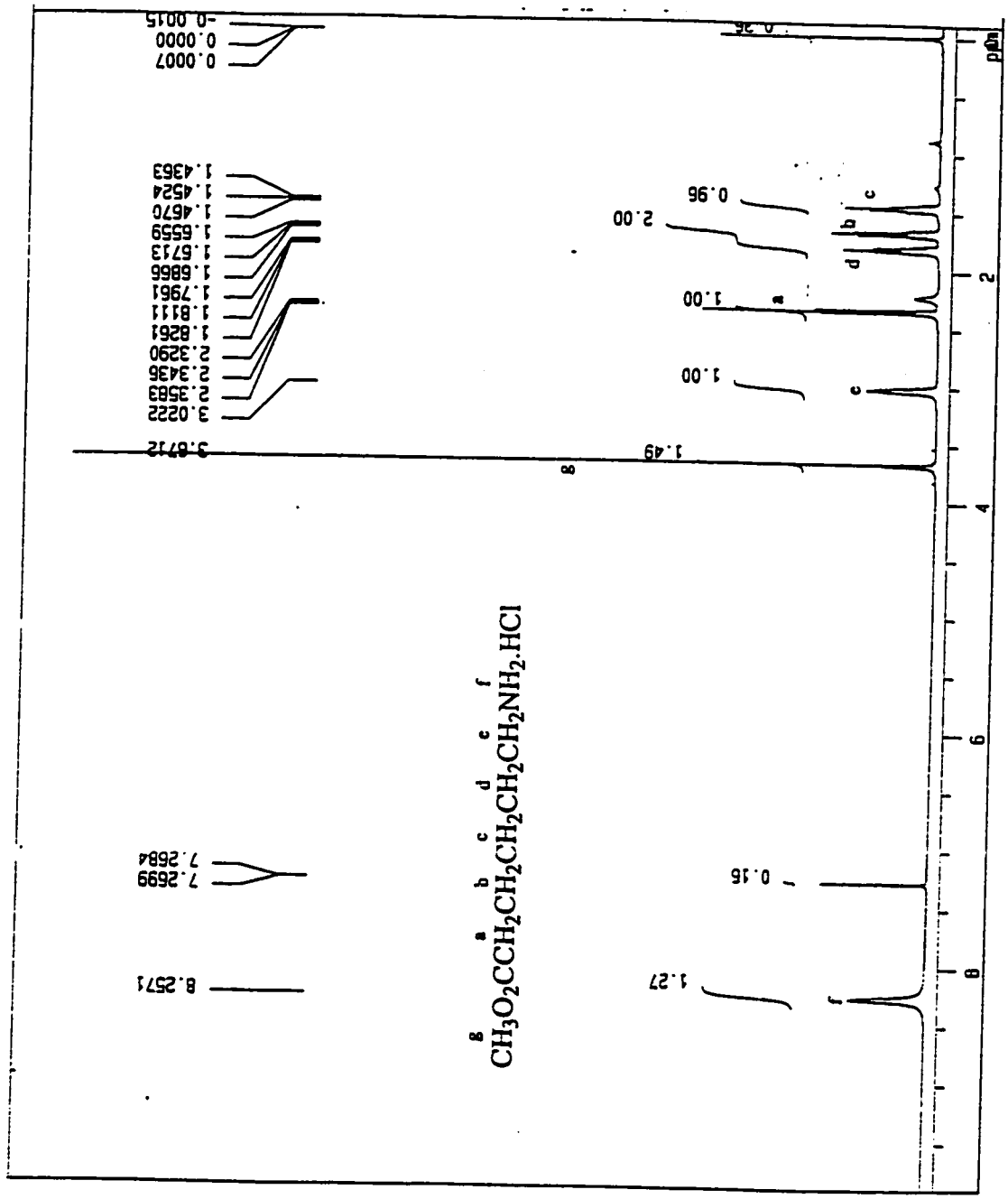



Figure 02 1H NMR spectrum of **(5)** in $CDCl_3$ at 20°C

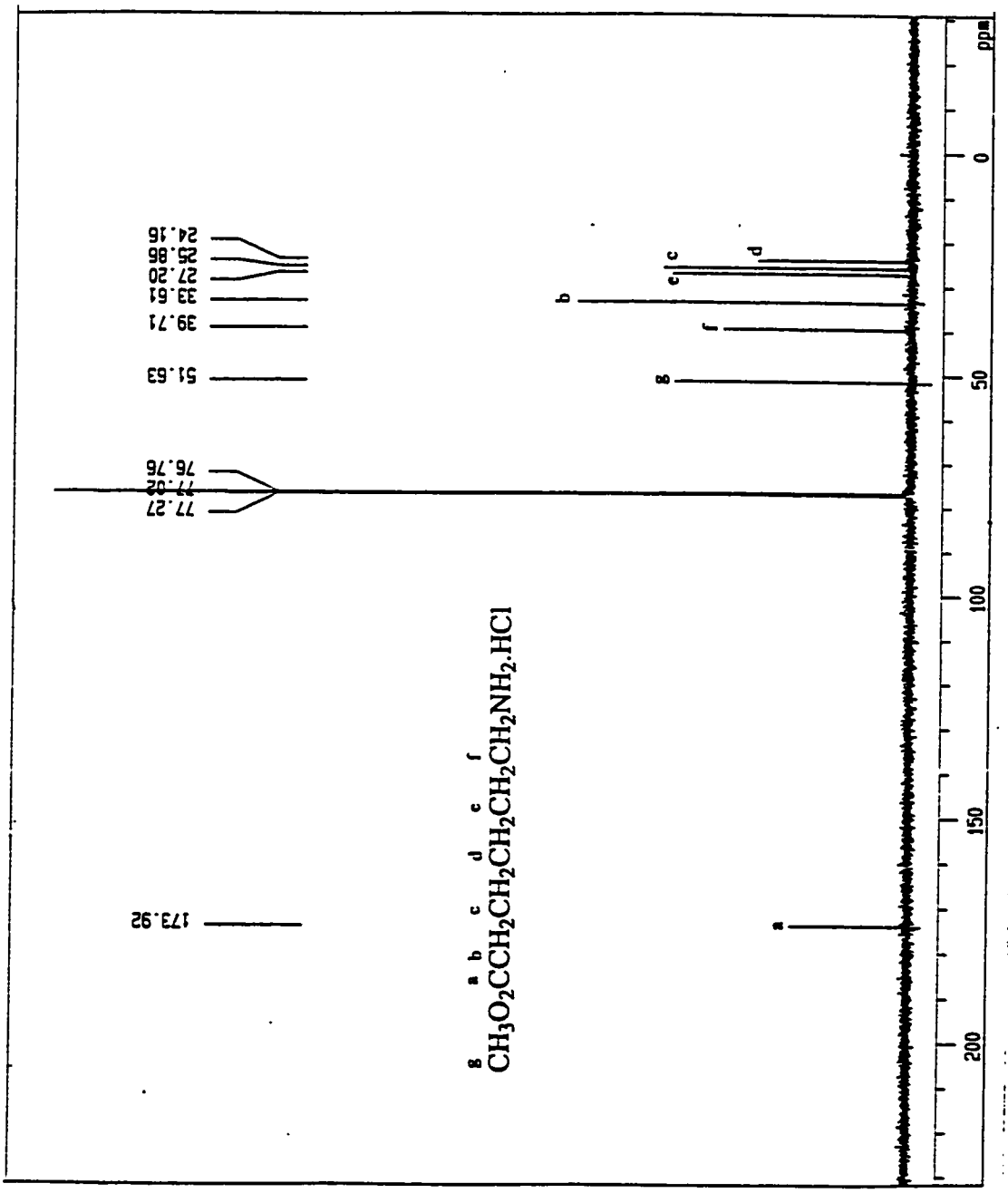



Figure 03 13C NMR spectrum of **(5)** in $CDCl_3$ at 20°C

Figure 1. The absorption at 1734 $cm^{-1}$ indicates the presence of the ester functionality. The $^{1}H$ NMR and $^{13}C$ NMR Spectra are shown in Figure 2 and 3.

The amine **(5)** on treatment with 2 equivalents of allyl chloride yielded methyl-6-(*N,N*-diallyl amino) hexanoate **(6)** with 60% yield. Tables 1 and 2 summarize the different reaction conditions that were tried. Allyl bromide was used as reagent and sodium hydroxide (in Table 1) and potassium carbonate (in Table 2) as the base. Maximum yield obtained using allyl bromide is 40% (Entry 4, Table 1; Entry 2, Table 2).

The low yield of the reactions using allyl bromide compared to the yield when allyl chloride was used is evident from the tables. This is mainly due to the facile formation of the triallyl quaternary ammonium salt as almost 30% of the product. This reflects the better leaving group ability of the bromide group.

The FTIR spectrum of **(6)** (Figure 4) shows absorption at 1743 $cm^{-1}$ (indicating ester functionality) and the absorptions at 1645 $cm^{-1}$ and 3075 $cm^{-1}$ are characteristic of the olefinic groups. The $^{1}H$ NMR and $^{13}C$ NMR Spectra shown in Figures 5 and 6 confirm the structure of **(6)**.

**TABLE 1: Results of preparation of (6)[a] using sodium hydroxide as base.**

| Entry No. | MeOH (mL) | Time (hour) | Temp. (°C) | Yield (%) |
|---|---|---|---|---|
| 1 | 50 | 20 | 25 | 24 |
| 2 | 110 | 4 | 25 | 25 |
| 3 | 75 | 5÷15 | 0/25 | 30 |
| 4 | 75 | 6.5 | 25 | 40 |

[a]150 mmol amine (5) , 300 mmol allylbromide, and 450 mmol sodium hydroxide were used in all reactions.

**TABLE 2: Results of preparation of (6)[a] using Potassium carbonate as base.**

| Entry No. | Solvent | Solvent volume (mL) | Time (hour) | Temp (°C) | Yield (%) |
|---|---|---|---|---|---|
| 1 | MeOH | 50 | 22+2 | 25/45 | 25 |
| 2 | MeOH | 100 | 18 | 45 | 40 |
| 3 | $H_2O$ | 25 | 5 | 25 | 20 |
| 4 | $Et_2O$ / $H_2O$ | 100/30 | 3 | 25 | 36 |

[a]150 mmol amine **(5)** , 300 mmol allylbromide, and 225 mmol potassium carbonate were used in all reactions.

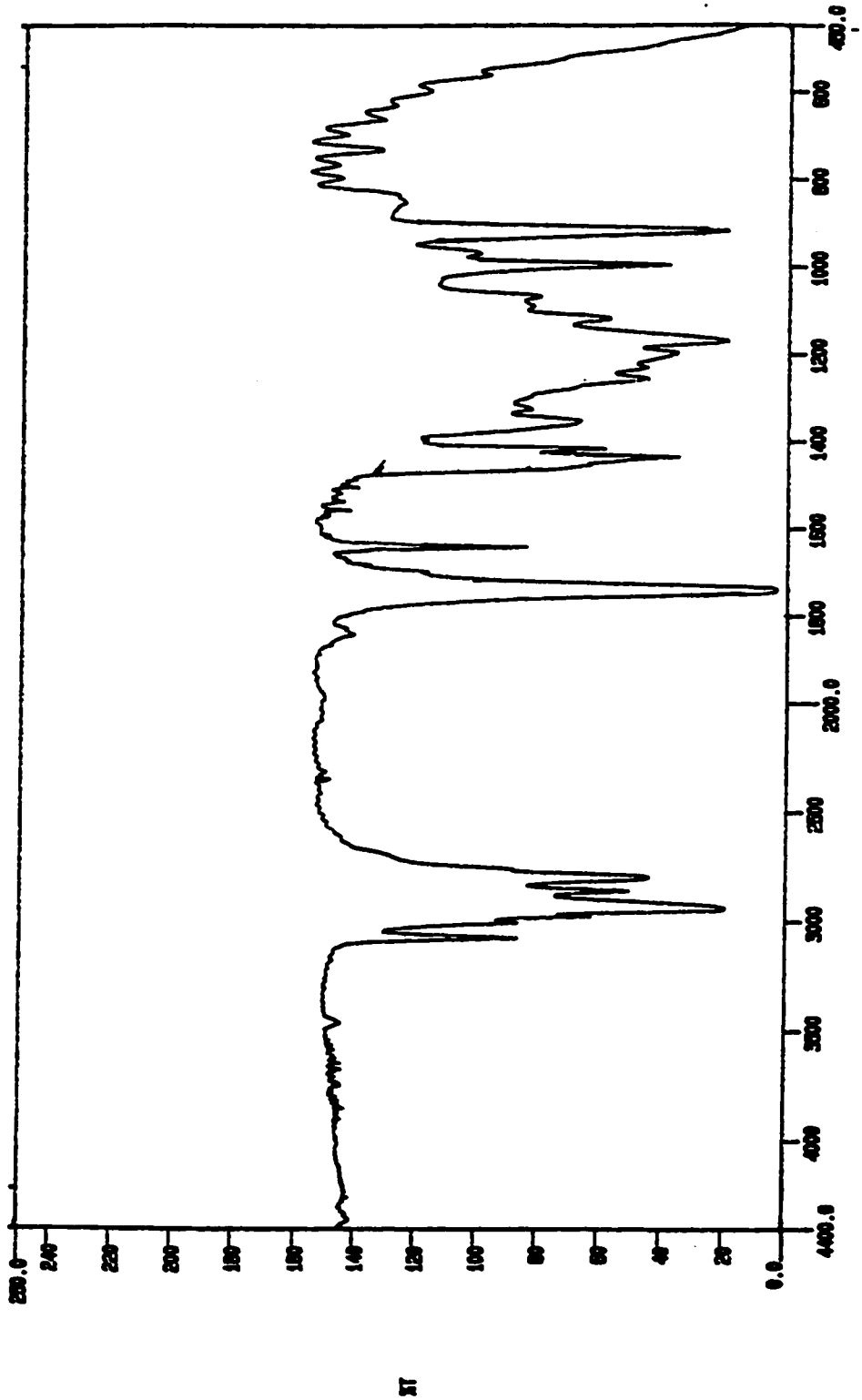



Figure 04 FTIR spectrum of (6) in KBr at 20°C

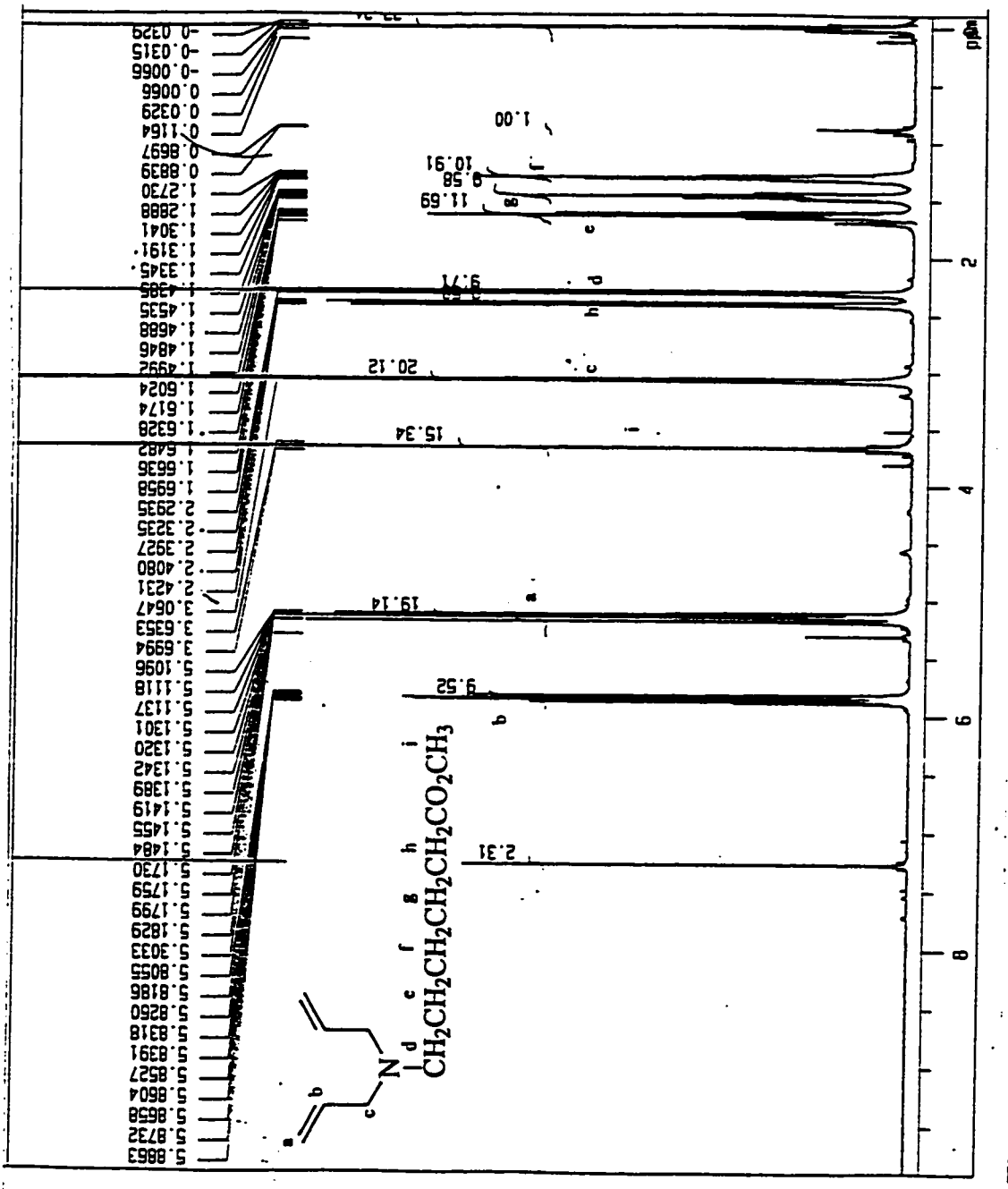



Figure 05 1H NMR spectrum of (6) in $CDCl_3$ at 20°C

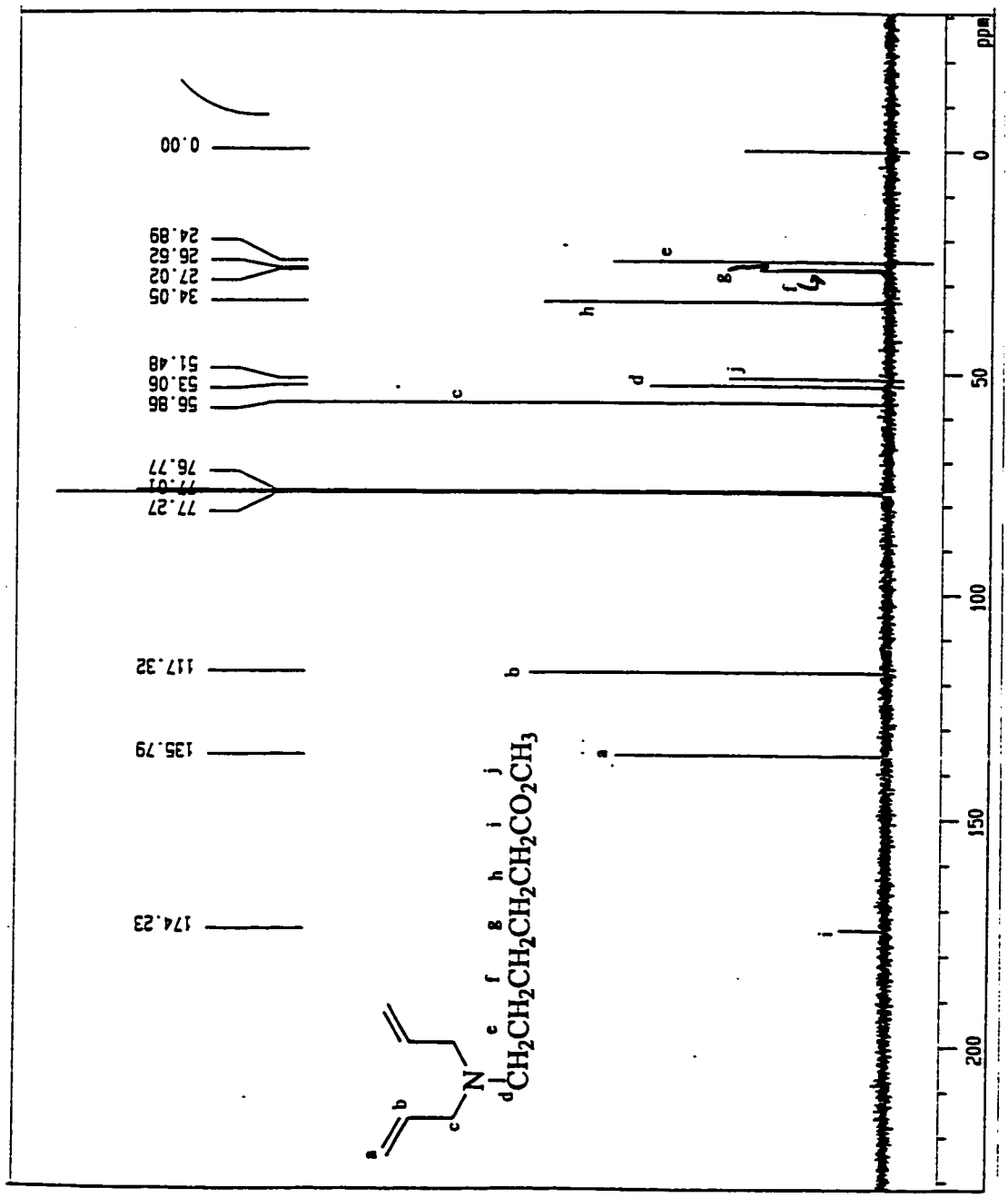



Figure 06 13C NMR spectrum of **(6)** in $CDCl_3$ at 20°C

The quaternary ammonium salt (**7**) was obtained by treatment of (**6**) with ethyl chloroacetate at 50°C. The reaction conditions employed are summarized in Table 3. It is evident that the reaction proceeds satisfactorily in the absence of solvent. Excess ethylchloroacetate was used in all of the reactions. Highest yield of 75% was obtained at 50°C and 72 hours reaction time (Entry 3, Table 3). The monomer (**7**) is a hygroscopic viscous liquid. It was found to be soluble in methanol, acetone and water. The I.R spectra showed absorptions at 1740 $cm^{-1}$ which indicates the presence of the ester functionality. Strong peak at 3370 $cm^{-1}$ indicates OH absorption due to water showing the hygroscopic nature of the monomer. The FTIR spectrum is shown in Figure 7. The $^{1}H$ NMR and $^{13}C$ NMR spectra, shown in Figures 8 and 9, confirm the structure of the monomer. The DEPT, COSY and CHSHF spectra of the monomer are shown in Figures 10, 11 and 12, respectively. These spectra were used to facilitate the assignment of peaks in the $^{1}H$ NMR spectrum of the monomer. The DEPT experiment allows the assignment of the methyl, methylene, and methine protons. The CHSHF spectrum allows assignment of the peaks in the $^{13}C$ NMR spectrum by correlation with peaks in the $^{1}H$ NMR spectrum.

**TABLE 3: Results of quaternarization reaction.**

| Entry No. | Dially amine (mmol) | $ClCH_2CO_2Et$ (mmol) | Time (hour) | Temp. (°C) | Yield (%) |
|---|---|---|---|---|---|
| 1 | 90 | 450 | 120+148 | 30/40 | 60 |
| 2 | 90 | 450 | 48 | 40 | 60 |
| 3 | 90 | 450 | 56 | 50 | 70 |
| 4 | 90 | 450 | 72 | 50 | 75 |
| 5 | 90 | 234 | 48 | 60 | 35 |

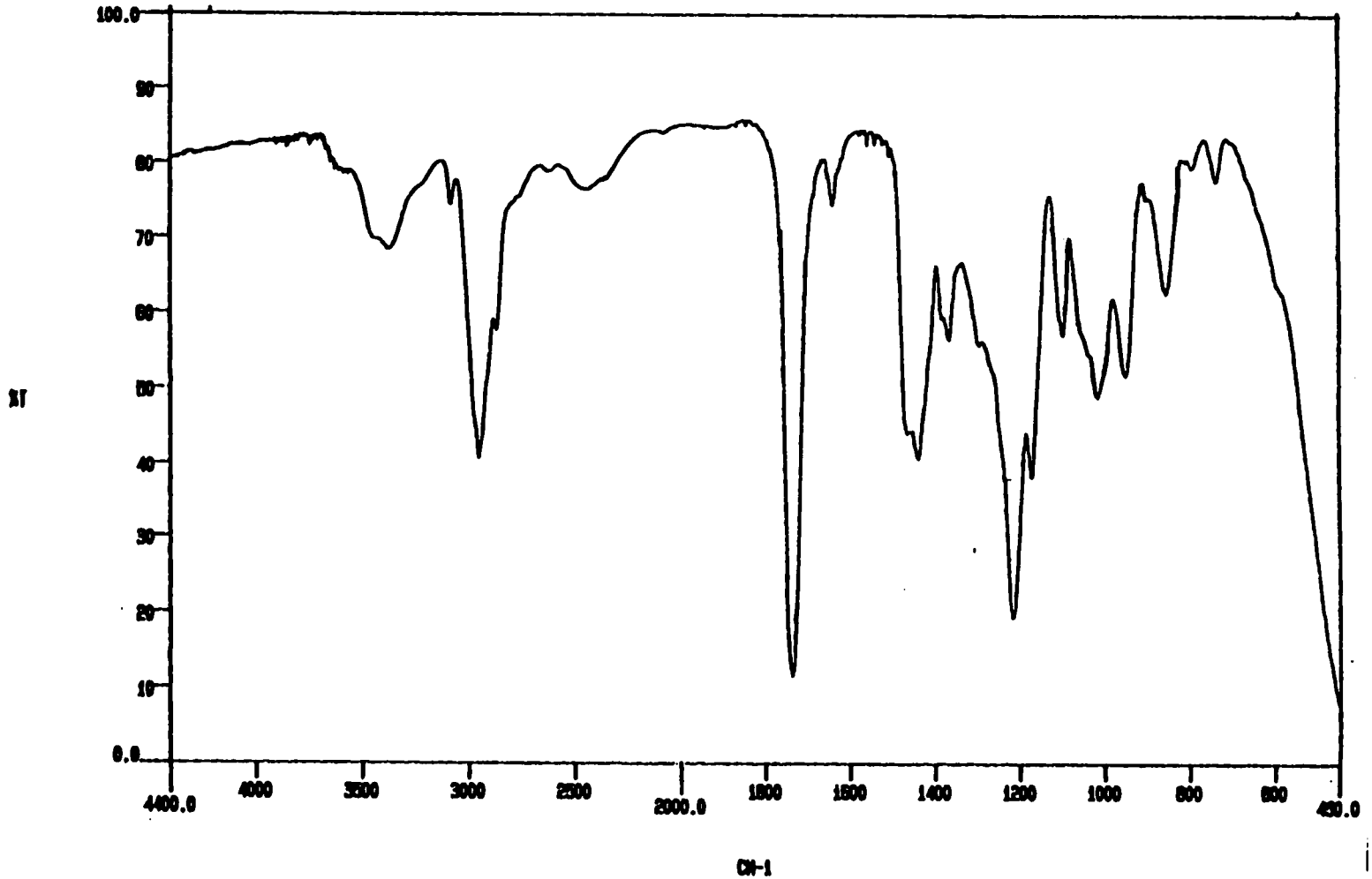



Figure 07 FTIR spectrum of **(7)** in KBr at 20°C

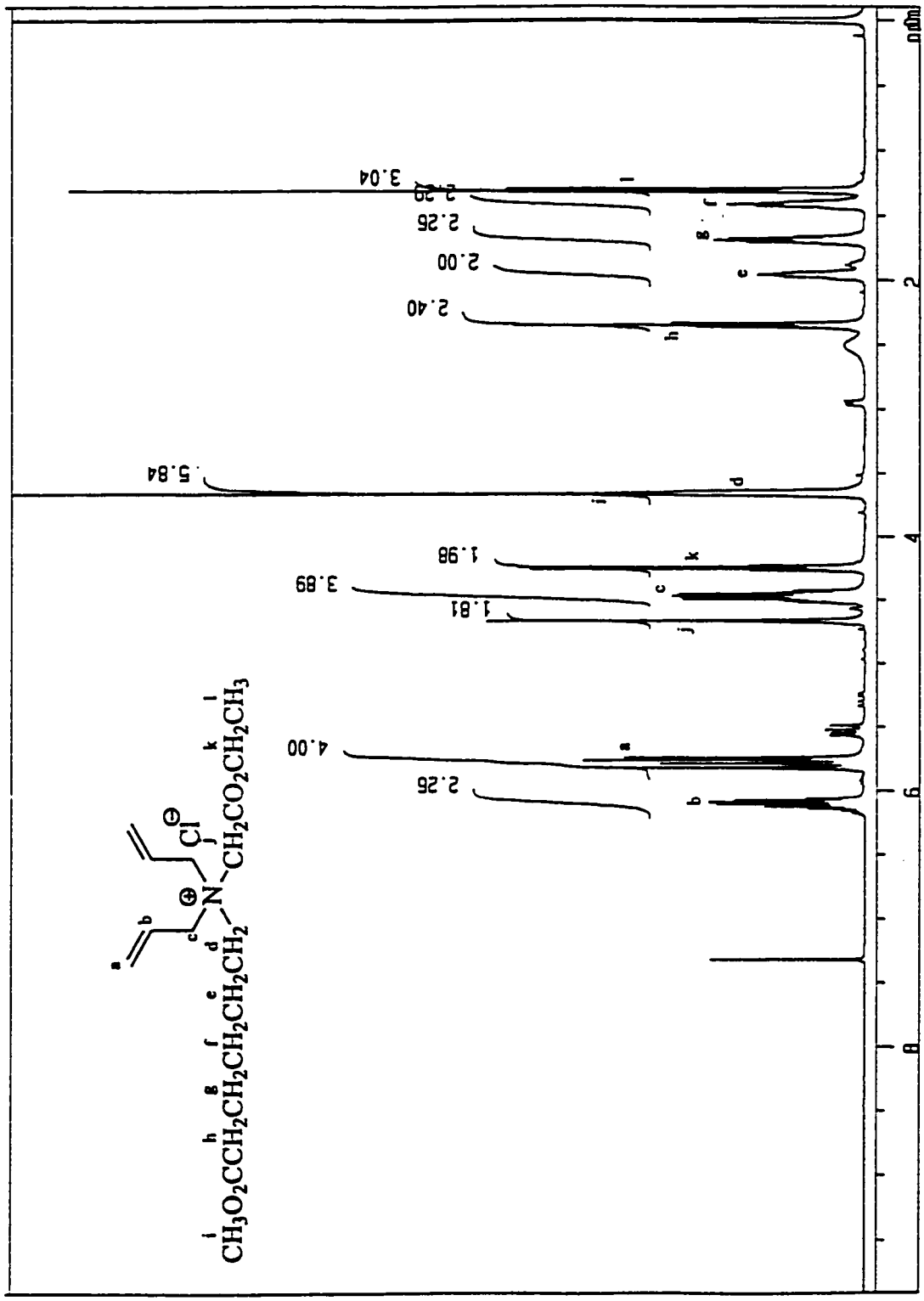



Figure 08 1H NMR spectrum of (7) in $CDCl_3$ at 20°C

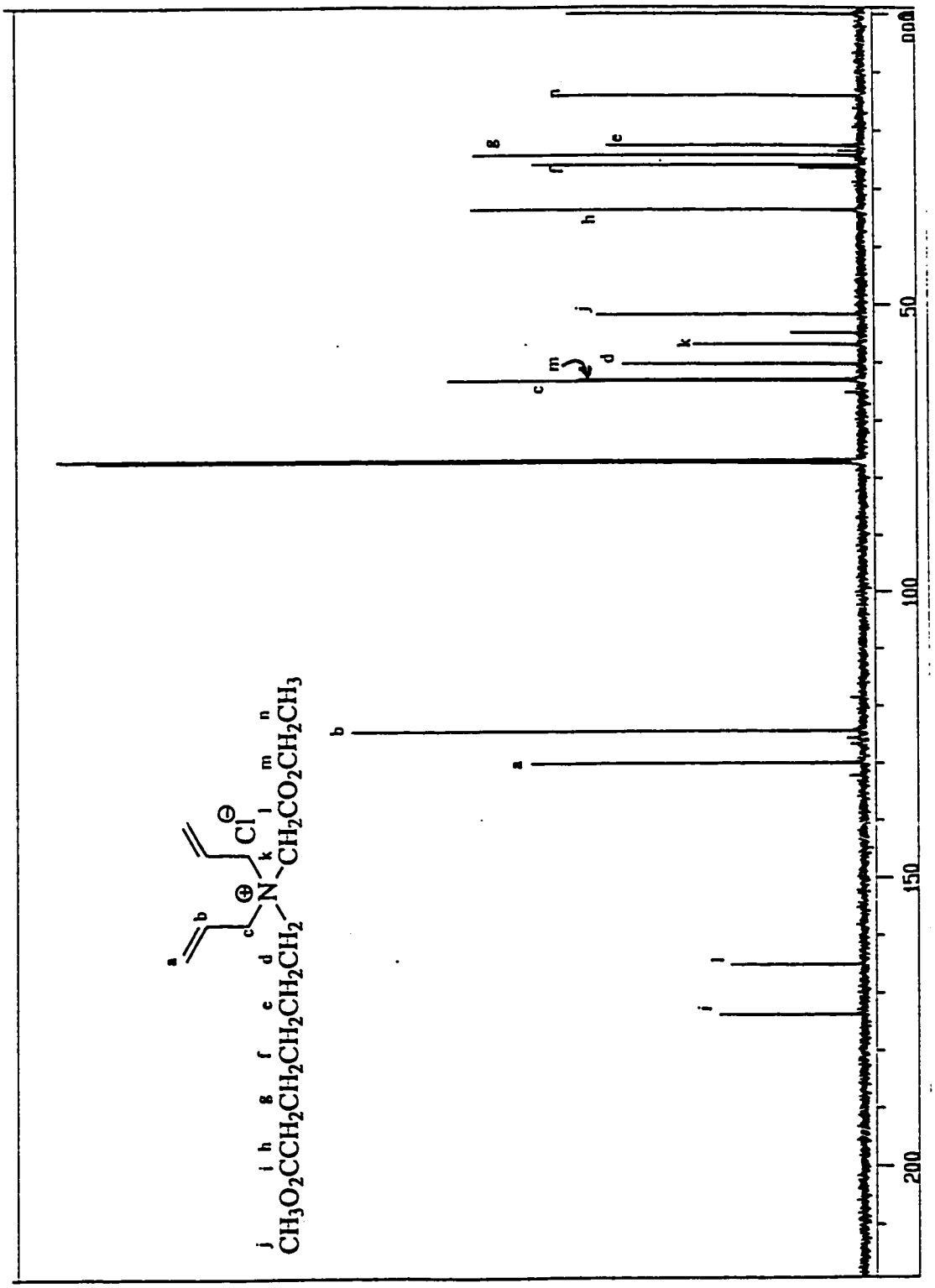



Figure 09 13C NMR spectrum of (7) in $CDCl_3$ at 20°C

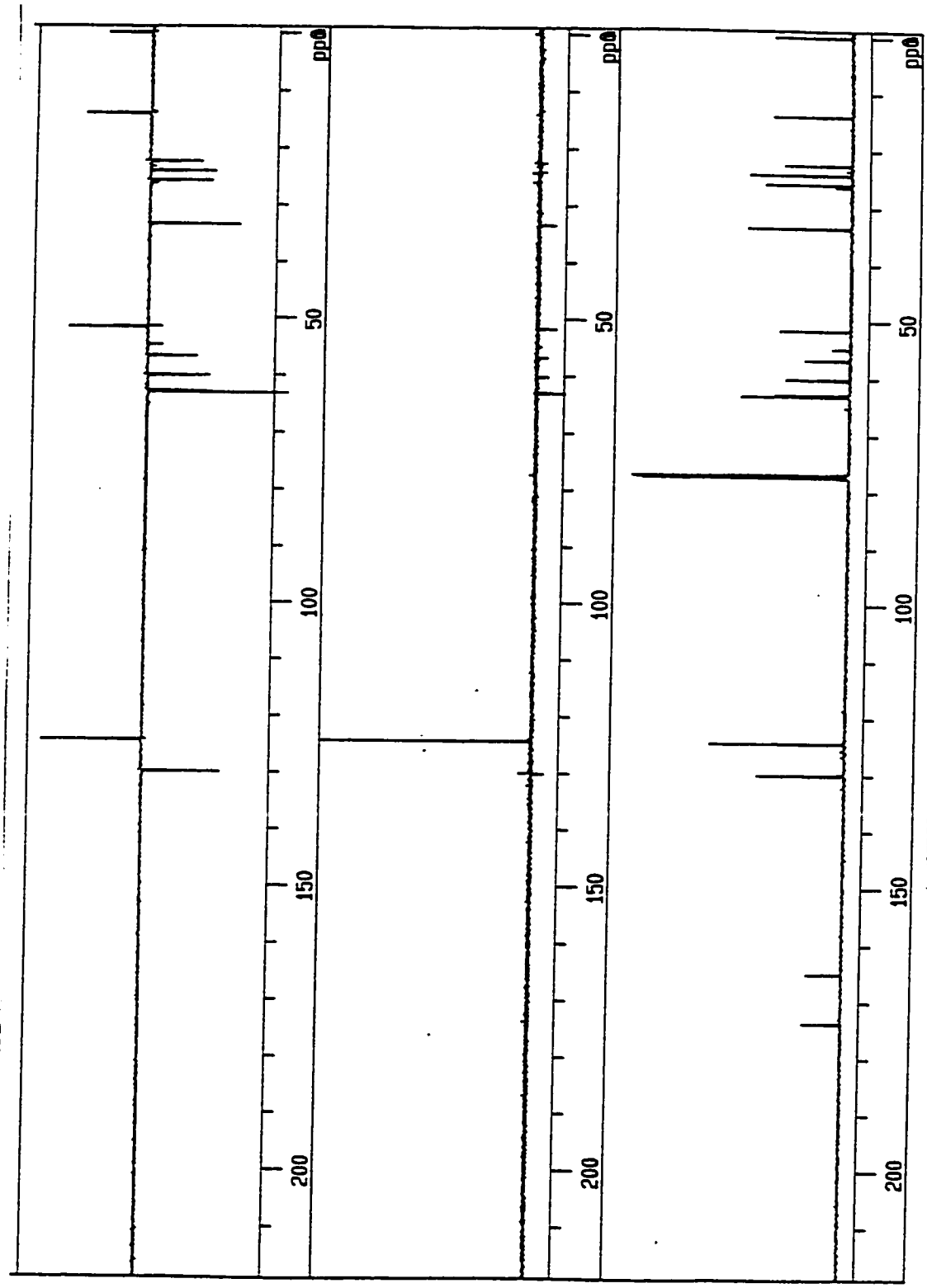



Figure 10 DEPT NMR spectrum of (7) in $CDCl_3$ at 20°C

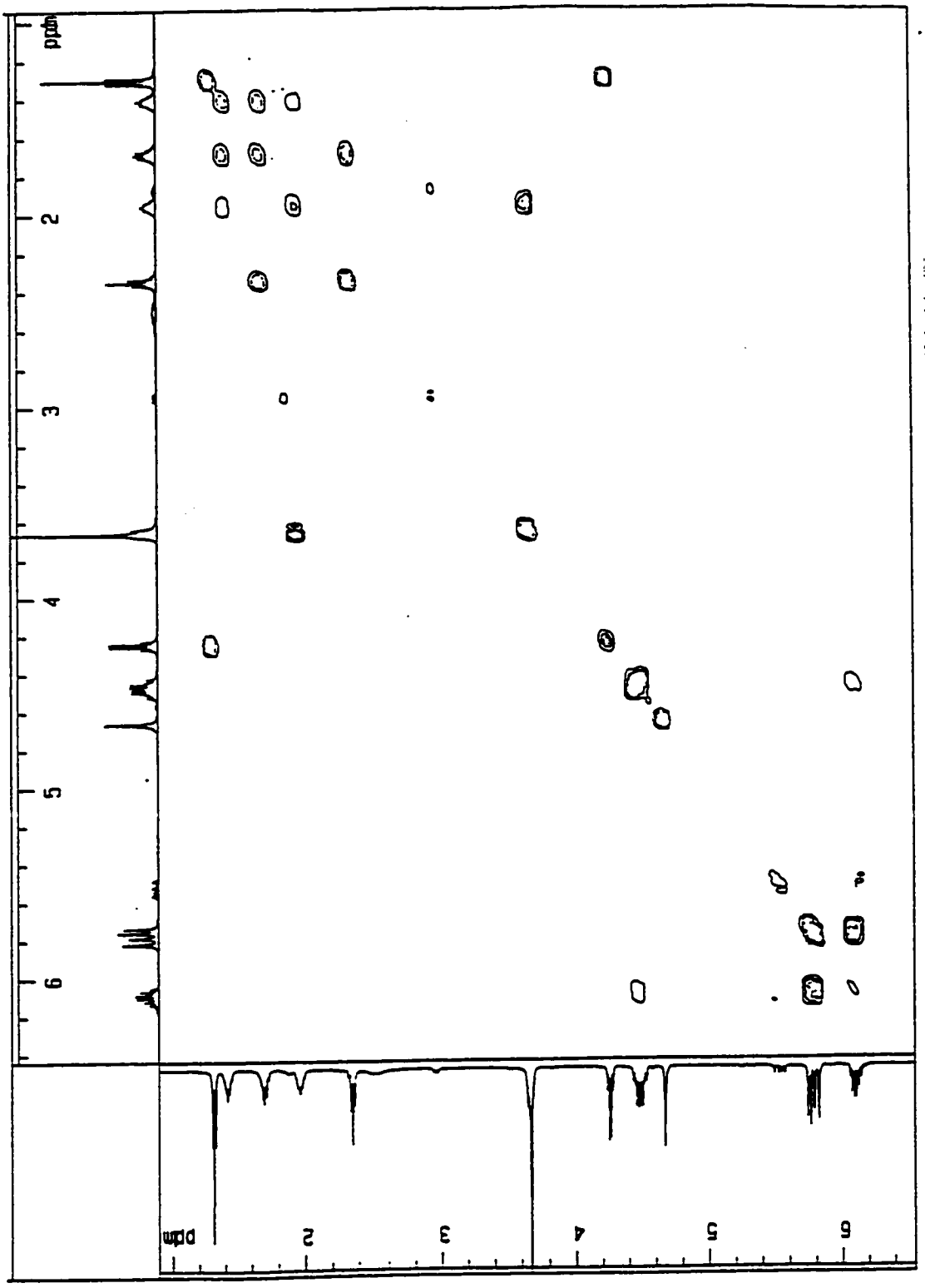



Figure 11 COSY 2D-NMR spectrum of (7) in $CDCl_3$ at 20°C

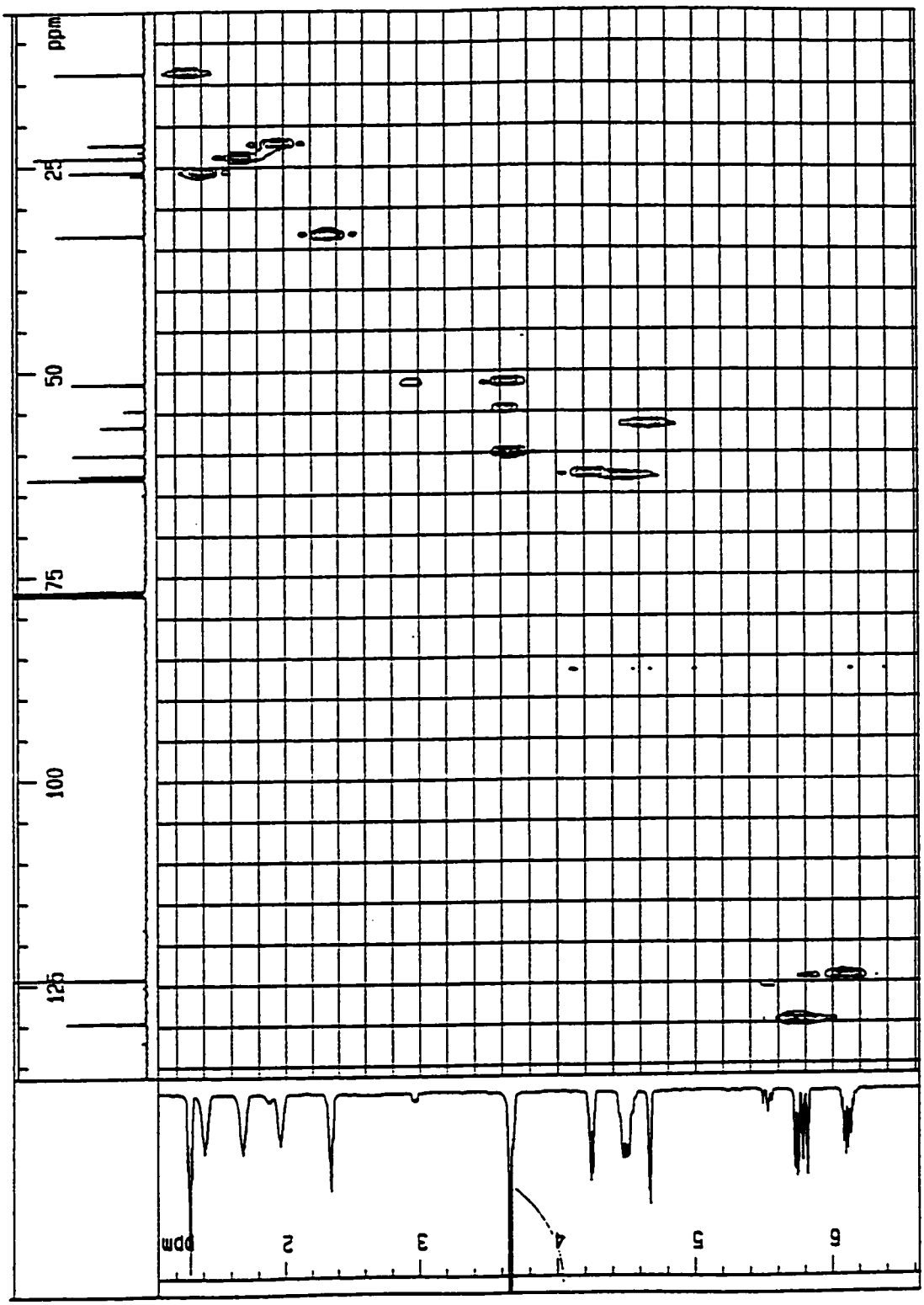
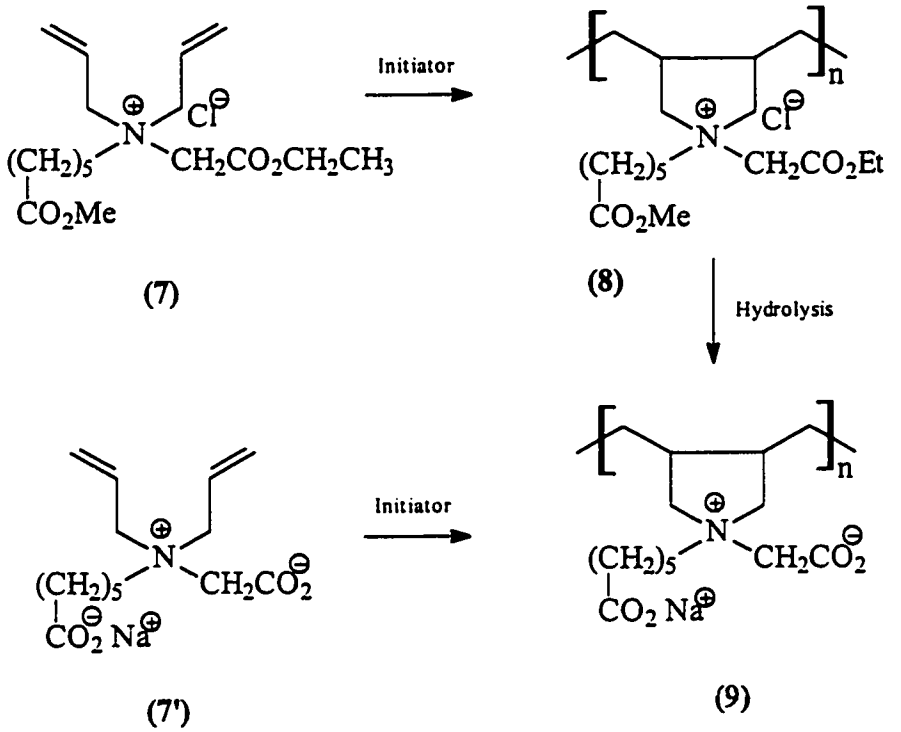



Figure 12 CHSHF 2D-NMR spectrum of (7) in $CDCl_3$ at 20°C

## 3.2 Synthesis and characterization of homopolymer (8)

The monomer (7) was polymerized to the polyelectrolyte (8), which was then hydrolysis to yield the zwitterionic polymer (9) as shown in Scheme 2.




**Scheme 8**

Since Ali[32] has reported successful hydrolysis of a similar polyelectrolyte, no attempt was made to synthesize the zwitterionic monomer (7') that could serve as an alternative precursor to polyampholyte (9). Polymerization of (7) was attempted in water (monomer concentration 65% w/w) using ammonium persulfate as initiation at 70°C as described by Ali for the polymerization of *N,N*-diallyl-*N*-carboethroxy methyl-N-methyl ammonium chloride. However, no polymer was obtained and other initiator/solvent systems were attempted. These included hydrogen peroxide in water and azobisisobutyronitrile in

dimethylsulfoxide (DMSO). Both these attempts failed. Successful polymerization occurred in water (monomer concentration 70% w/w) using tertiary butylhydroperoxide as initiator at 75°C as described by Butler[34] for the polymerization of diallyl dimethyl ammonium chloride.

The results of the polymerization using different initiator concentrations are summarized in Table 4. The highest intrinsic viscosity was obtained for polymerization reaction under Entry no.1 with an initiator concentration of 10 mg/g of monomer. The polyelectrolyte **(8)** was found to be highly soluble in water and methanol and slightly soluble in acetone. The pH of 1% solution of polyelectrolyte was found to be 3.30. Figure 13 and Figure 14 show the FTIR and $^{1}H$ NMR spectra of polymer **(8)**. Absorption at 1748 $cm^{-1}$ indicates the presence of ester group. The hygroscopic nature of the homopolymer is revealed by the strong absorption at 3454 $cm^{-1}$. $^{1}H$ NMR spectrum confirms the structure of the repeating unit. The $^{13}C$ NMR spectrum of the polymer is shown in Figure 15.

The homopolymers are cream colored hygroscopic solids melting in the range 134°C to 149°C with the color darkening above 215°C indicating the onset of thermal decomposition. The Differential Thermal Analysis and Thermal Gravimetric Analysis of a homopolymer sample (Entry 5, Table 4) are shown in Figure 16.

**TABLE 4: Results of Homopolymerization reaction[a].**

| Entry No. | Monomer Conc. (w/w) | TBHP[b] Conc. (mg/g Monomer) | Yield (%) | $\eta_{sp}/C$ (dL/g) |
|---|---|---|---|---|
| 1 | 65 | 10 | 59 | 0.165 |
| 2 | 70 | 10 | 60 | 0.136 |
| 3 | 70 | 15 | 63 | 0.075 |
| 4 | 70 | 20 | 75 | 0.056 |
| 5 | 83 | 10 | 60 | 0.146 |
| 6 | 90 | 10 | 40 | 0.141 |

[a]Polymerization reactions were carried out in aqueous medium at 50°C for 18 hours followed by 75°C for 48 hours.
[b]TBHP= tertiary butylhydroperoxide.

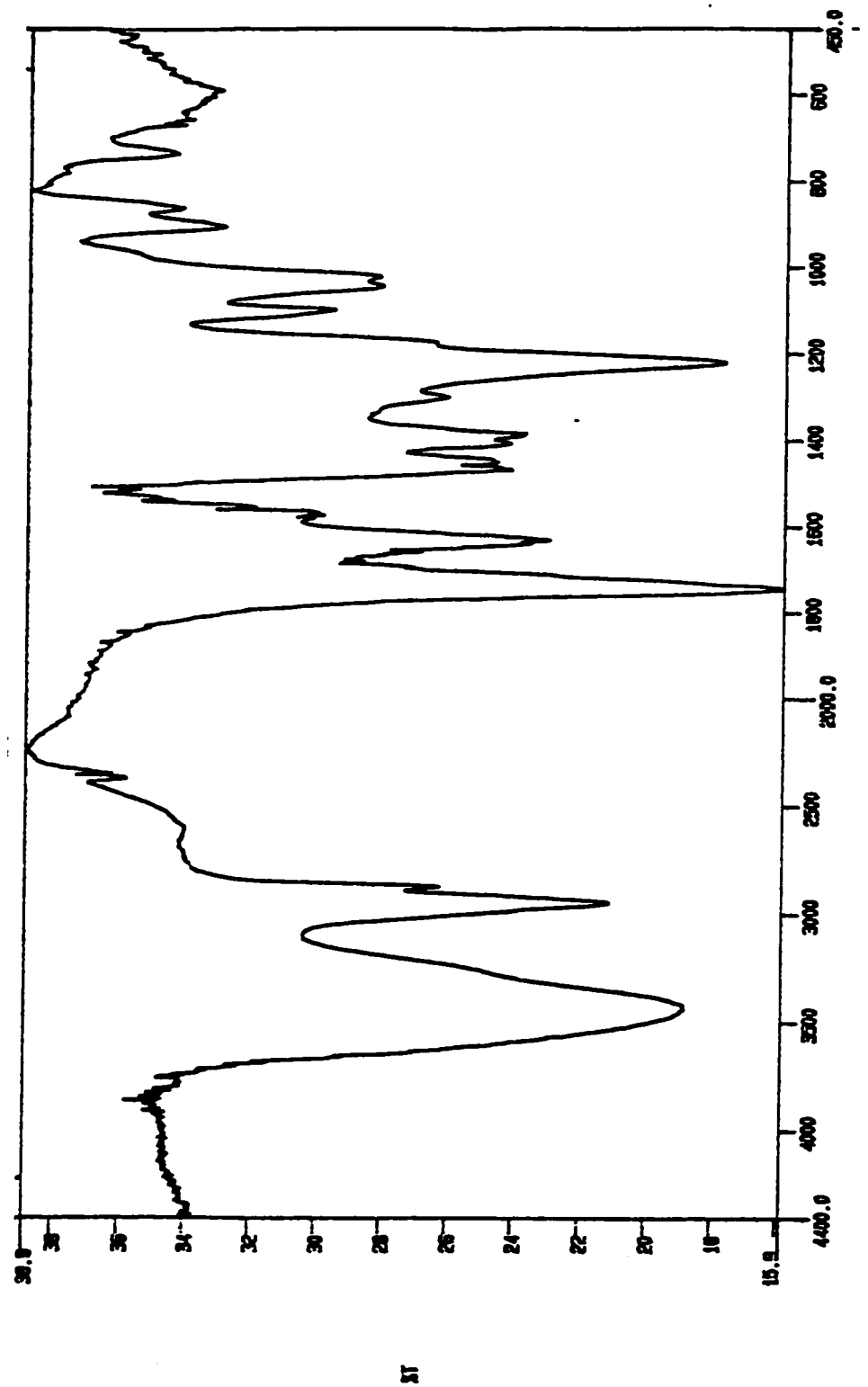



Figure 13 FTIR spectrum of polymer (8) in KBr at 20°C

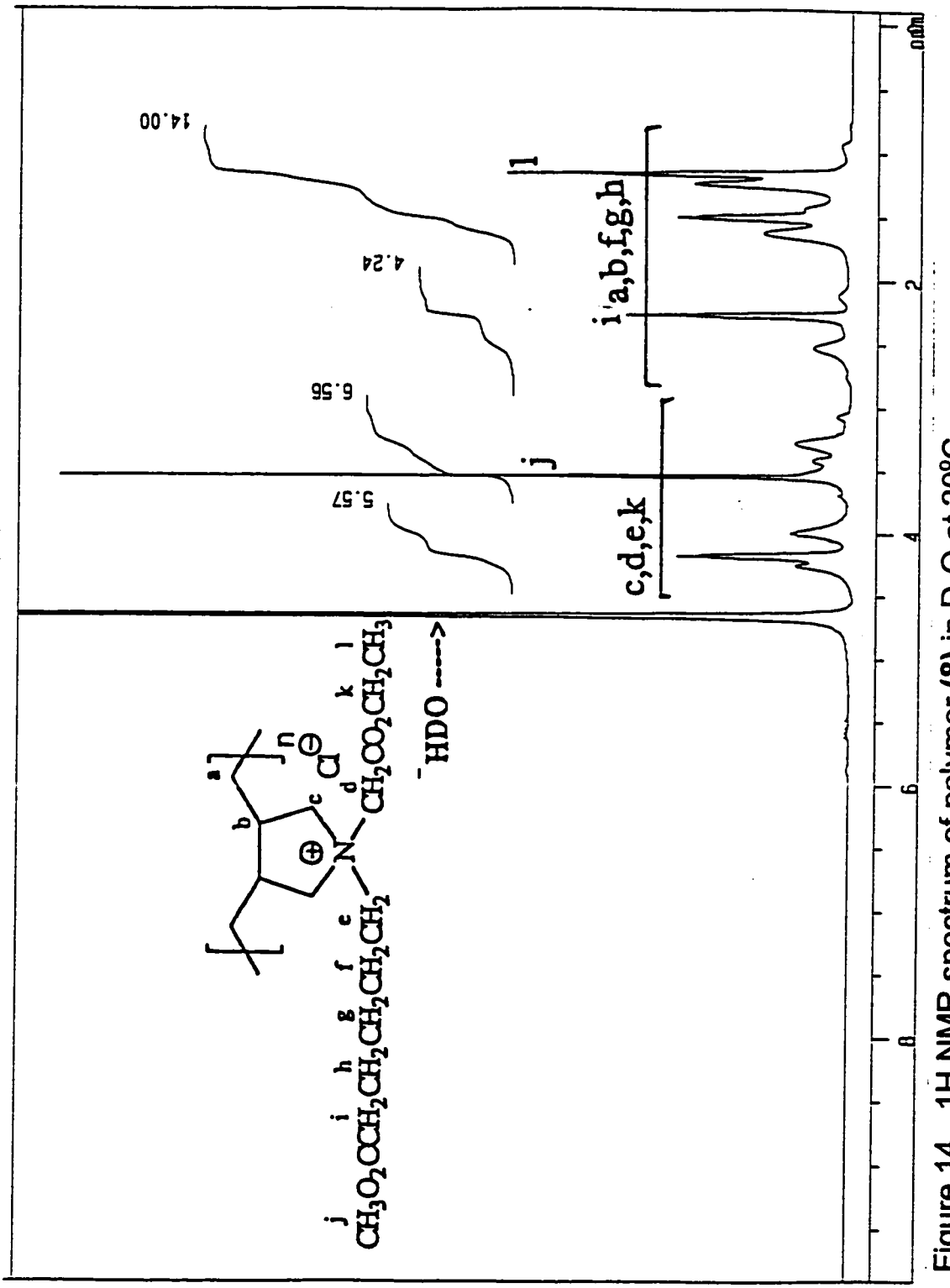



Figure 14 1H NMR spectrum of polymer (8) in $D_2O$ at 20°C

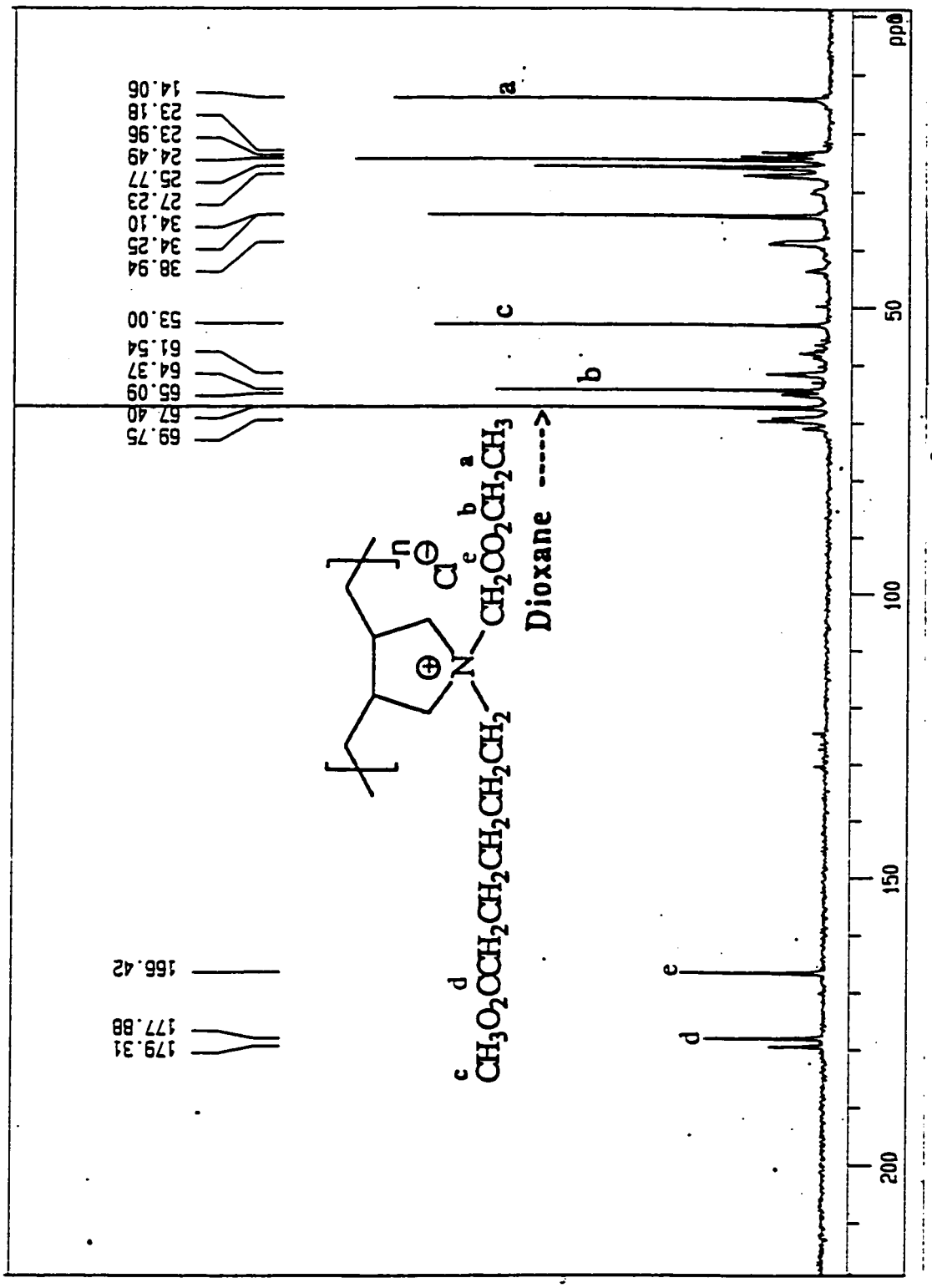



Figure 15 13C NMR spectrum of polymer (8) in $D_2O$ at 20°C

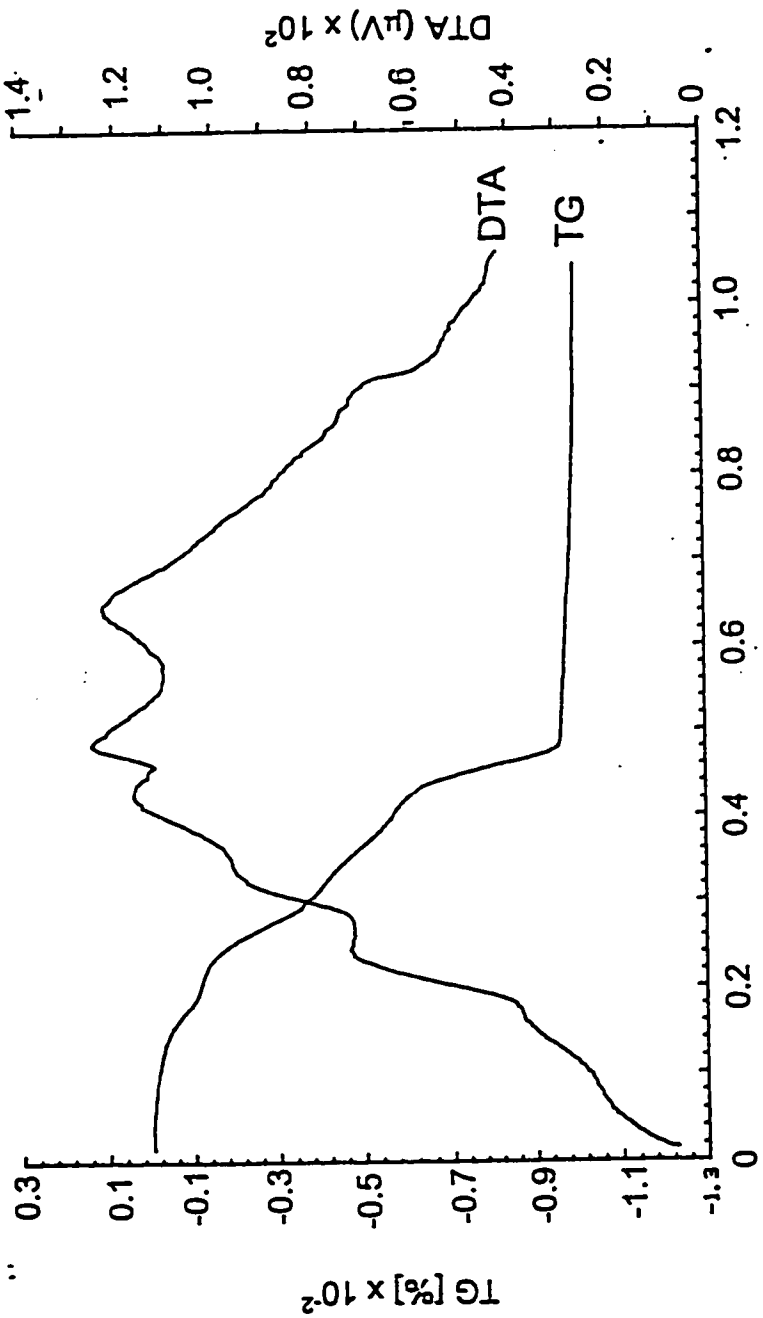



Figure 16 DTA/TG thermograms of polymer **(8)**

The viscosity behavior of the dilute aqueous solution of a homopolymer sample (Entry number 5, Table 4) is shown in Figure 17. Homopolymer **(8)** being a cationic polyelectrolyte exhibits viscosity behavior typical of linear charged polymers i.e., its reduced viscosity increases concave upwards as the polymer solution in water is diluted as seen in Figure 17. In dilute solution the counter ion on charged polymer chains diffuses out of the intramolecular region into the intermolecular solvent medium. By doing so, the mobile counter ions leave a net positive charge within the domain of the molecule. The electrostatic repulsive forces between the charges in the polymer backbone cause the polymer chain to adopt a greatly expanded configuration thereby increasing the hydrodynamic volume. This effect on the configuration manifests itself in a large increase in the intrinsic viscosity ($\eta_{sp}/C$). However this rise in the intrinsic viscosity is finite because as a result of the diffusion of mobile counter ions into the surrounding medium a net positive charge builds up within the macromolecular domain and the potential within the molecule is increased relative to the surroundings. A state of equilibrium is eventually reached in which the potential is just enough to support the difference in the concentration of ions inside and outside the molecular domain.

Figures 18 - 23 show the viscosity behavior of homopolymer samples (Entries 1 - 6, Table 4) in aqueous 0.1 N NaCl solution. Figure 24 shows the viscosity behavior of homopolymer sample (Entry 3, Table 4) in aqueous 0.2 N NaCl. A comparison of figure 20 and 24 shows that the intrinsic viscosity of the polyelectrolyte homopolymer **(8)** is strongly dependent on the concentration of added electrolyte i.e., NaCl. The addition of electrolyte to the solvent medium causes the ionic concentration gradient to be reversed and it is no longer favorable for the counter ions to diffuse outside the intramolecular

domain. As ions diffuse in the reverse direction a new equilibrium is established in which there is no net charge within the intramolecular domain. The absence of repulsive electrostatic forces leads to the collapse of the expanded macromolecular configuration and therefore a drop in hydrodynamic volume. This is manifested in a reduction of the intrinsic viscosity with increasing salt concentration as evidenced by the viscosity data above.

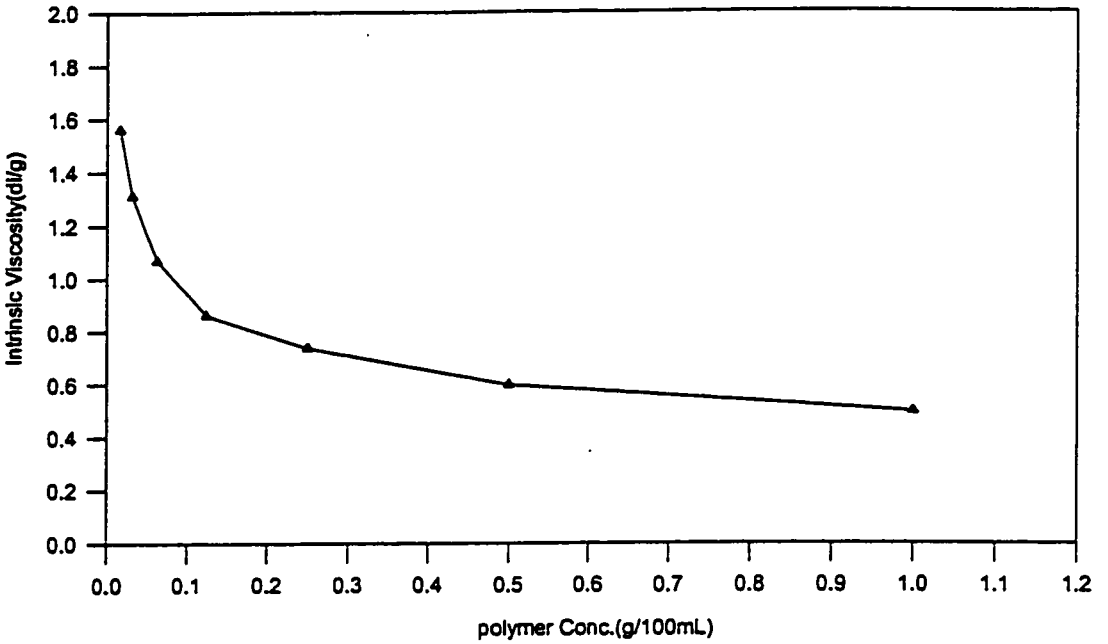



Figure 17 Viscosity behavior of homopolyelectrolyte **(8)** (Entry 5,Table 4) in deionized water at 30°C

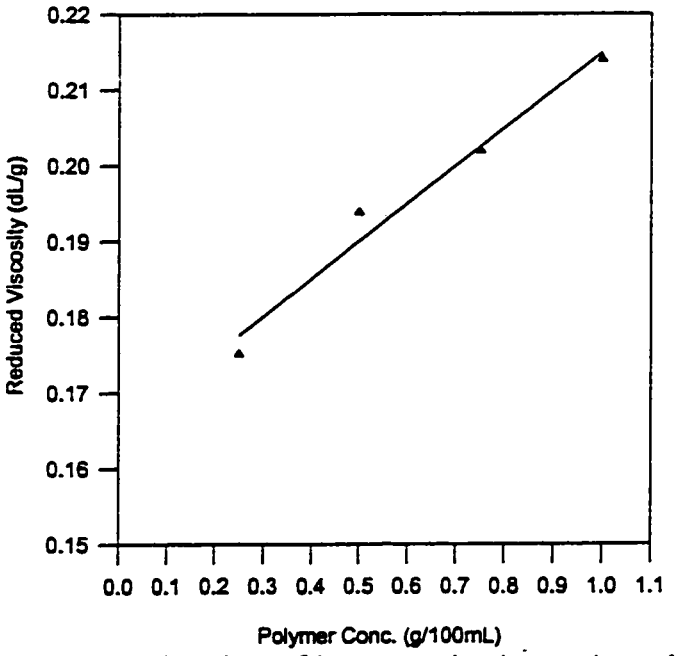



Figure 18 Viscosity behavior of homopolyelectrolyte **(8)** (Entry 1,Table 4) in 0.10 N NaCl solution at 30°C

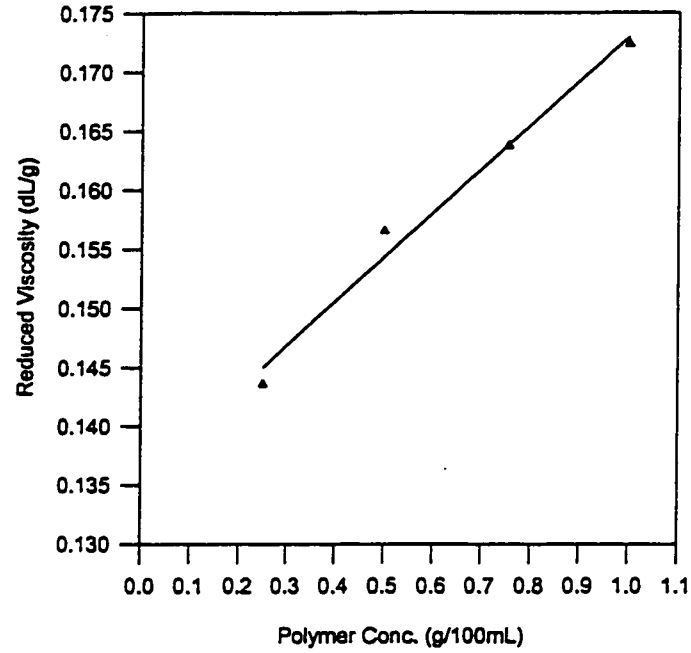



Figure 19 Viscosity behavior of homopolyelectrolyte **(8)** (Entry 2,Table 4) in 0.10 N NaCl solution at 30°C

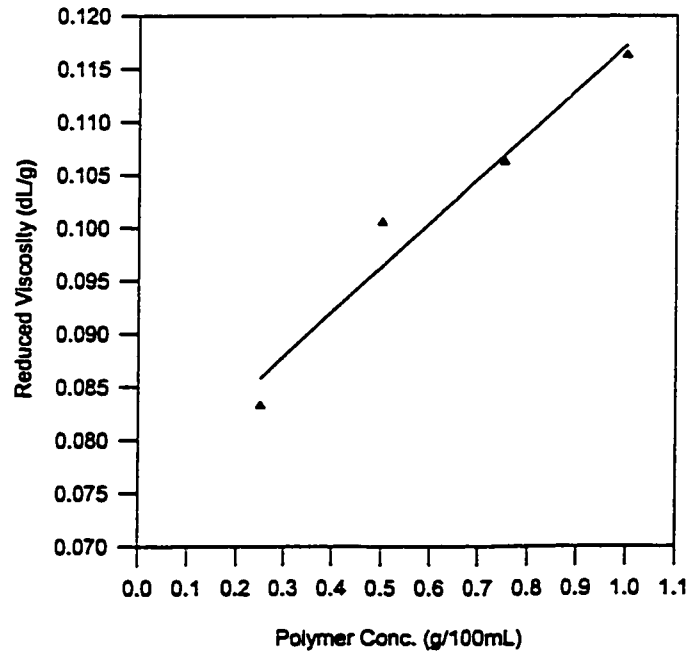



Figure 20 Viscosity behavior of homopolyelectrolyte **(8)** (Entry 3,Table 4) in 0.10 N NaCl solution at 30°C

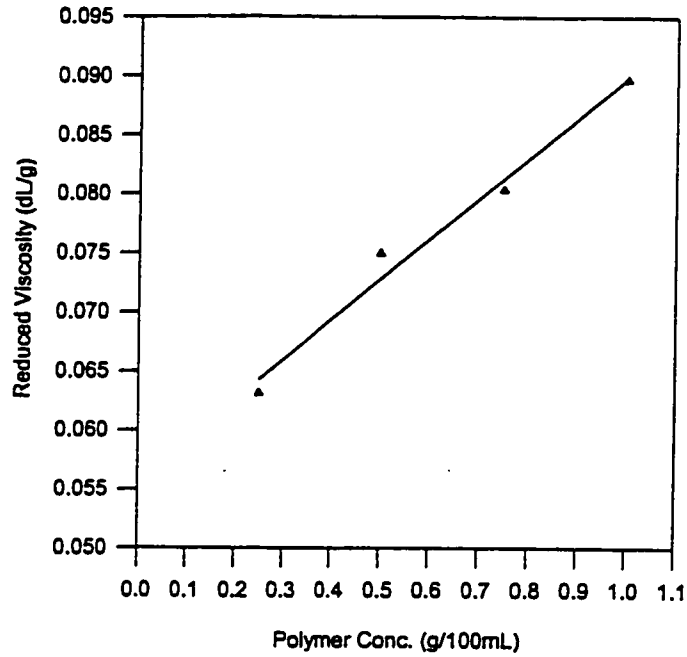



Figure 21 Viscosity behavior of homopolyelectrolyte **(8)** (Entry 4,Table 4) in 0.10 N NaCl solution at 30°C

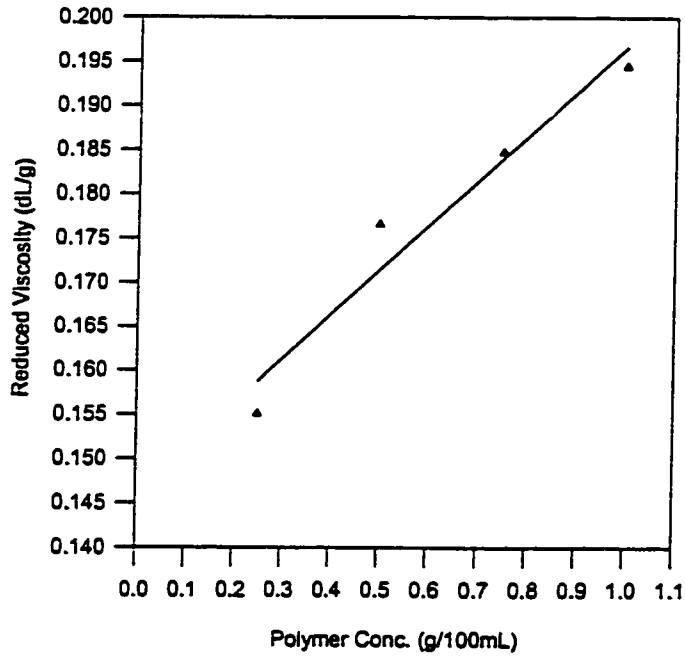



Figure 22 Viscosity behavior of homopolyelectrolyte **(8)** (Entry 5,Table 4) in 0.10 N NaCl solution at 30°C

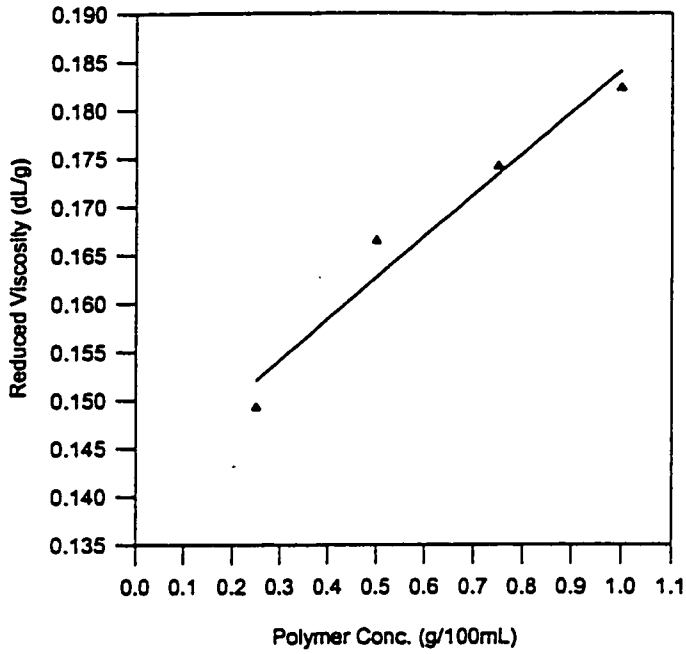



Figure 23 Viscosity behavior of homopolyelectrolyte **(8)** (Entry 6,Table 4) in 0.10 N NaCl solution at 30°C

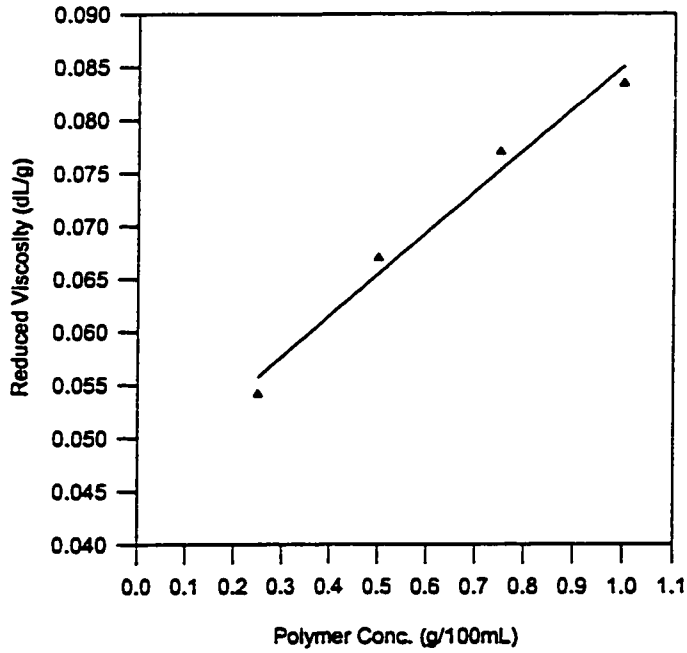
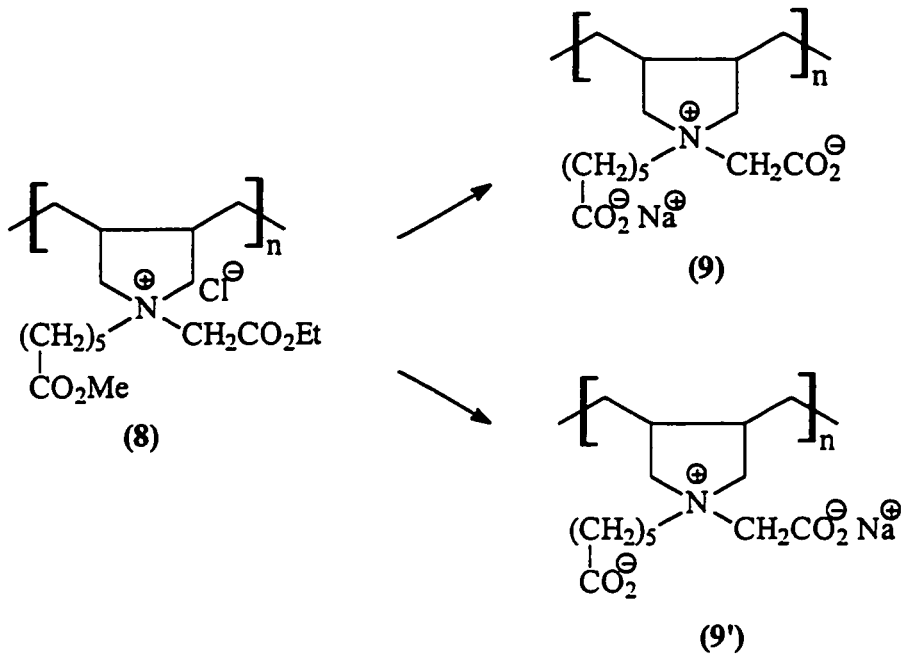



Figure 24 Viscosity behavior of homopolyelectrolyte **(8)** (Entry 3,Table 4) in 0.20 N NaCl solution at 30°C

## 3.3 Conversion of polyelectrolyte (8) to zwitterionic polyelectrolyte (9)




**Scheme 9**

Acid hydrolysis (6 N HCl, 40°C) of polyelectrolyte **(8)** was employed to convert the ester fuctionalities to carboxylic acids. The product was basified with sodium bicarbonate and dialyzed versus deionized water to give **(9)** and / or **(9')** in almost quantitative yield. The polymer was recovered by freeze-drying. The results of the hydrolysis reaction are summarized in Table 5.

The FTIR spectrum of **(9)** is shown in Figure 25. The absorption at 3429 $cm^{-1}$ arises from water indicating the hygroscopic nature of the polymer. The $^{1}H$ NMR and $^{13}C$ NMR spectra of polyelectrolyte **(8)** and zwitterionic polymer **(9)** are shown in Figure 26 and 27 respectively. As seen in Figures 26 and 27 the resonances for the $CH_3O$ and $CH_3CH_2O$

groups are absent in the spectra of **(9)** indicating that the complete hydrolysis of the polyelectrolyte **(8)** has been achieved.

The solubility of homopolymers **(8)** and **(9)** was determined in a series of common solvents covering a range of polarities. The results are shown in Table 6. Figure 28 shows the DTA/TG thermograms of polymer **(9)**.

As is evident from Scheme 3 both **(9)** and **(9')** are possible structures of the product. Structure **(9)** has greater validity because of the greater acidity of this carboxylate group relative to the carboxylate group on the other six-carbon chain. This greater acidity results from the higher stability of the carboxylate ion which in turn is a consequence of its proximity to the positively charged quaternary nitrogen. However what is more interesting is that fact that the structure of **(9)** has features characteristics of both of polyelectrolyte and polyampholytes. The $Na^+$, $CO_2^-$ ion pair should impart solution properties characteristics of the polyelectrolytes to polymer **(9)**, while the zwitterions comprising of the positive charge on the quaternary nitrogen and the negative charge on the carboxylic group should, in principle, impart to the polymer properties characteristics of the polyampholytes.

It was of interest to study the viscosity of this polymer to see whether the polymer would exhibit polyelectrolytic or anti-polyelectrolytic viscosity behavior. With this in mind, the viscosity of **(9)** in de-ionized water and in NaCl solutions of several concentrations were studied. The results are depicted in Figure 29 - 34. Figure 35 shows the variation of intrinsic viscosity with increasing NaCl concentration. Figure 29 shows

**TABLE 5: Results of hydrolysis reaction[a].**

| Entry No. | Time (days) | Temp. (°C) | Yield (%) | ηsp/C[b] PEA[c] | ηsp/C[b] PE[d] |
|---|---|---|---|---|---|
| 1 | 5 | 45 | 95 | 0.114 | 0.056 |
| 2 | 5 | 45 | 99 | 0.209 | 0.146 |

[a]5g polymer / 100mL 6N HCl was used in all hydrolysis reactions.
[b]Viscosity of 1-0.125 % polymer solution on 0.1 N NaCl at 30 °C was measured in Ubbelohde Viscometer (K=0.005989).
[c]PEA: Poly(electrolyte-ampholyte).
[d]PE: Polyelectrolyte.

**TABLE 6: Solubility of polymer (8) and (9).**

| Solvent | ε | (8) | (9) |
|---|---|---|---|
| Water | 78.4 | + | + |
| Methanol | 32.7 | + | + |
| Formic acid | 58.5 | + | + |
| Formamide | 111.0 | + | + |
| Ethylene glycol | 37.3 | + | + |
| Triethylene glycol | 23.7 | + | + |
| Acetic acid | 6.15 | + | + |

[a]2% (w/w) of polymer solution was made after the mixture was maintained at 70°C for 1 hour and then the temperature lowered to 23°C.
[b]'+' indicates soluble; '-' indicates insoluble; '±' indicates partially soluble

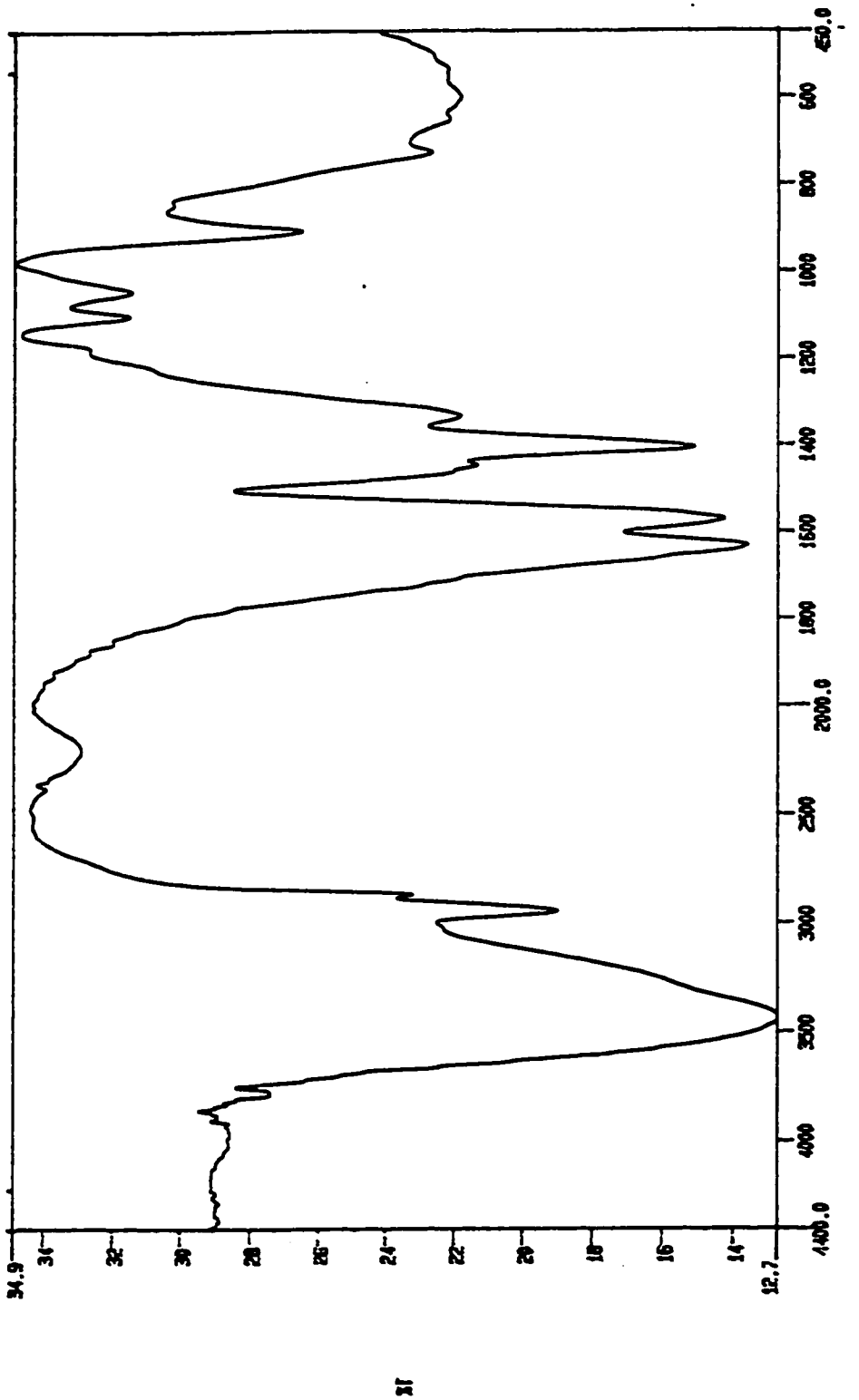



Figure 25 FTIR spectrum of polymer (**9**) in KBr at 20°C

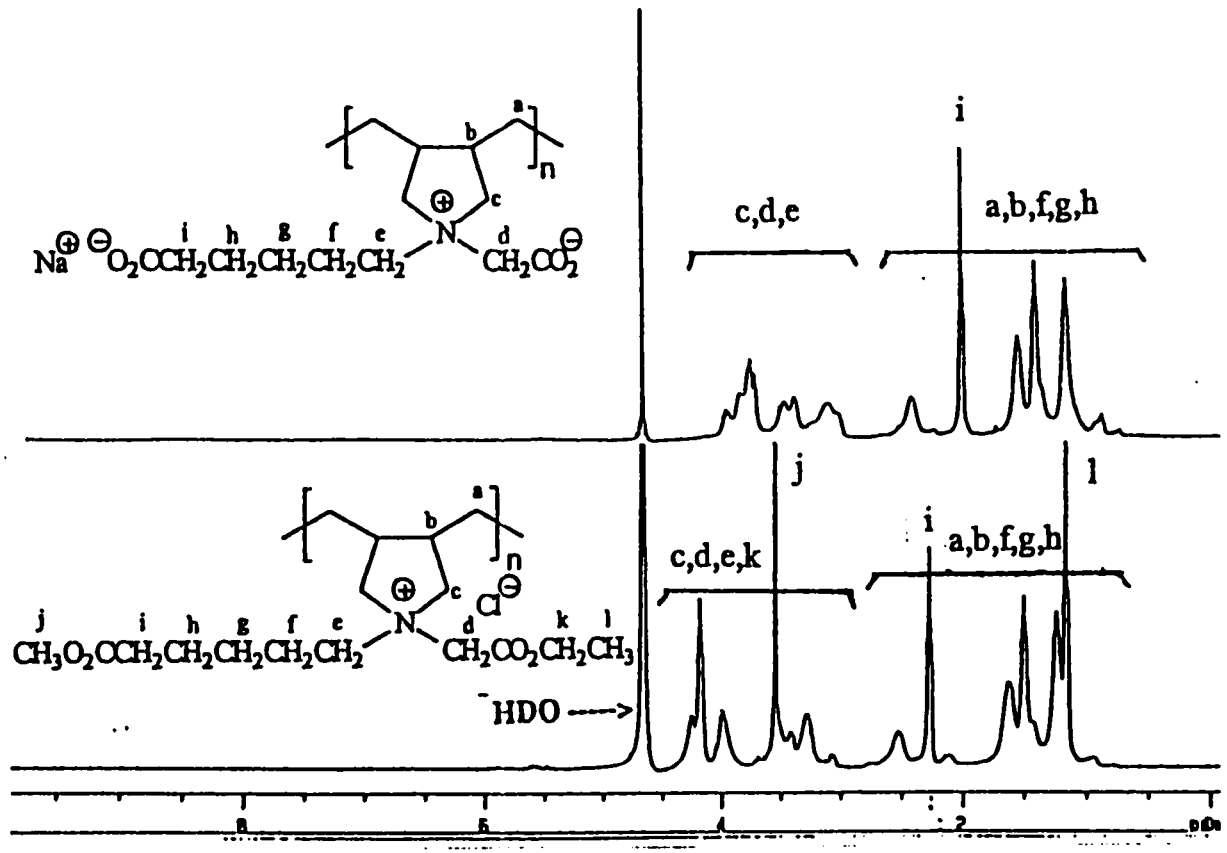



Figure 26 1H NMR spectra of polymer **(8)** and **(9)** in $D_2O$ at 20°C

(showing complete hydrolysis of the ester groups)

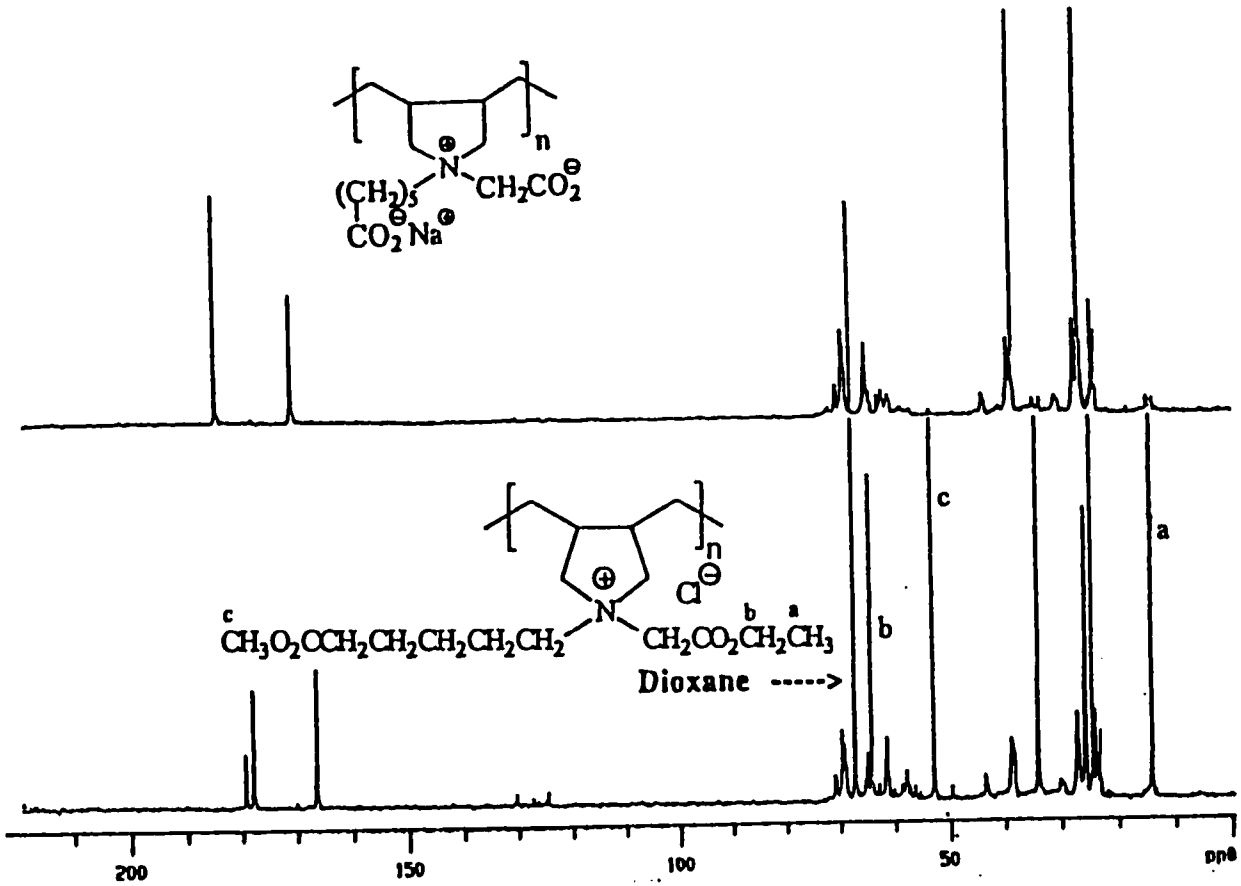



Figure 27 13C NMR spectra of polymer **(8)** and **(9)** in $D_2O$ at 20°C

(showing complete hydrolysis of the ester groups)

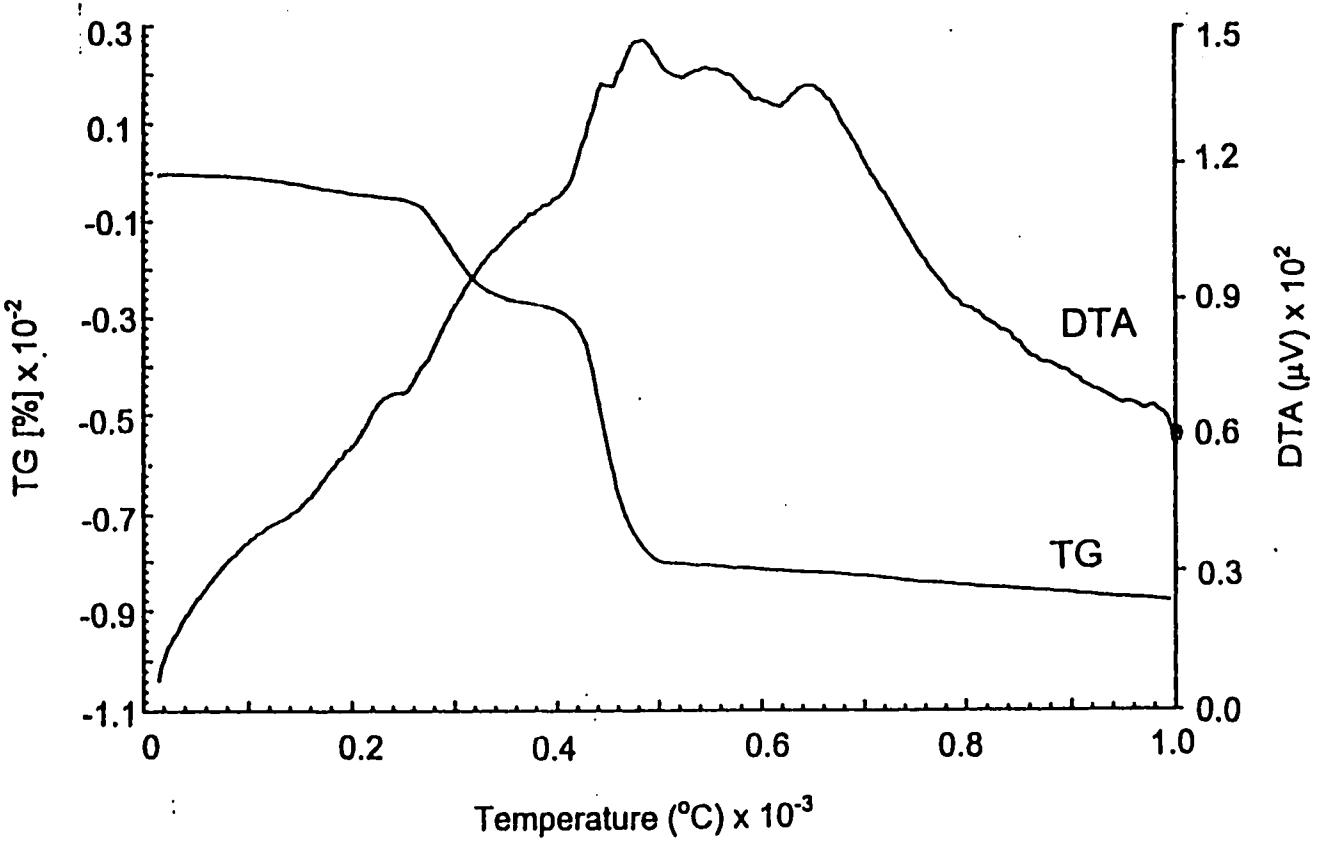



Figure 28 DTA/TG thermograms of polymer **(9)**

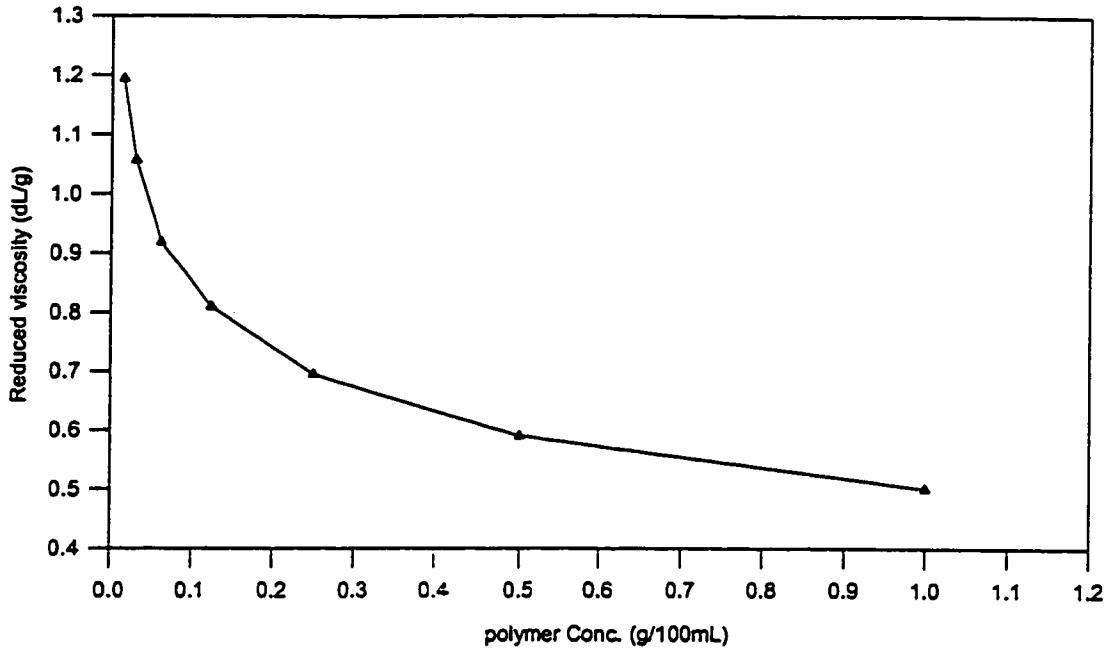



Figure 29 Viscosity behavior of zwitterionic polyelectrolyte **(9)** (Entry 2,Table 5) in deionized water at 30°C

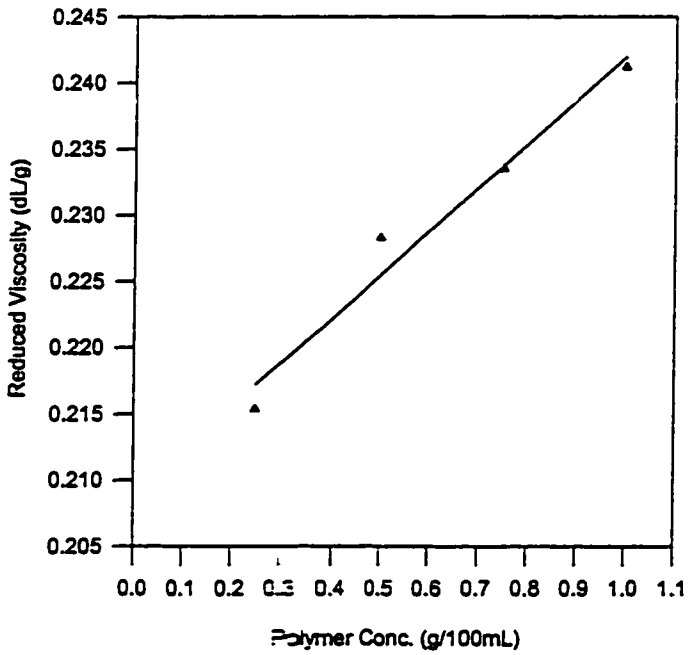



Figure 30 Viscosity behavior of zwitterionic polyelectrolyte **(9)** (Entry 2,Table 5) in 0.10 N NaCl solution at 30°C

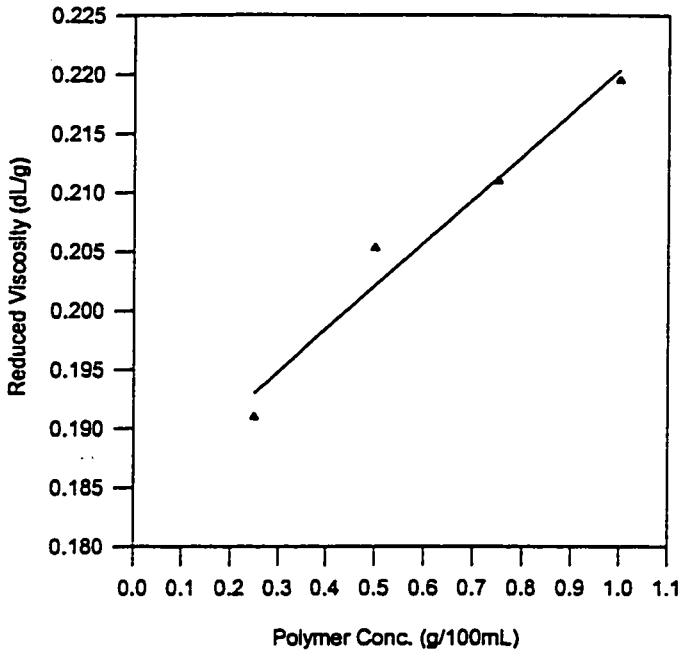



Figure 31 Viscosity behavior of zwitterionic polyelectrolyte **(9)** (Entry 2,Table 5) in 0.20 N NaCl solution at 30°C

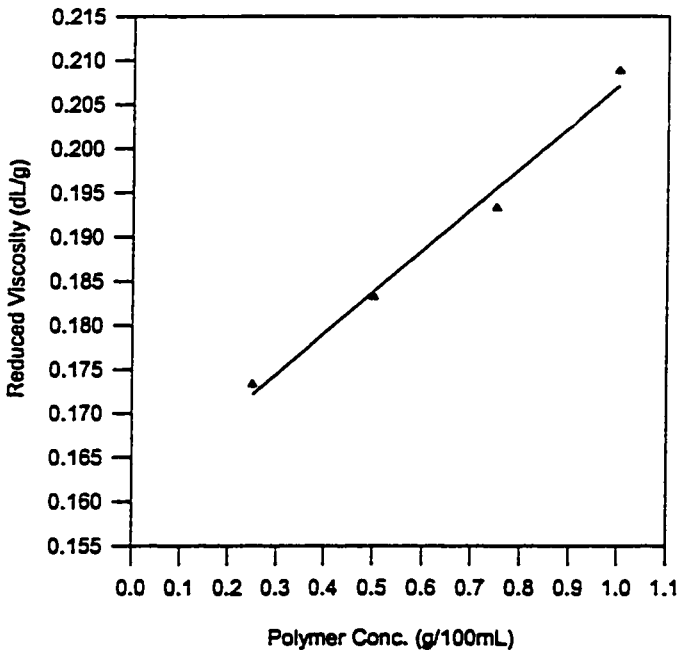



Figure 32 Viscosity behavior of zwitterionic polyelectrolyte **(9)** (Entry 2,Table 5) in 0.30 N NaCl solution at 30°C

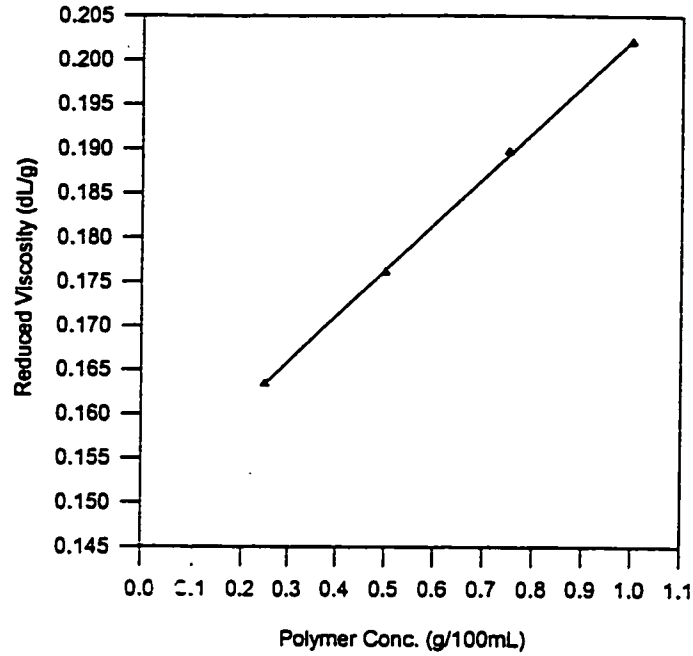



Figure 33 Viscosity behavior of zwitterionic polyelectrolyte **(9)** (Entry 2,Table 5) in 0.50 N NaCl solution at 30°C

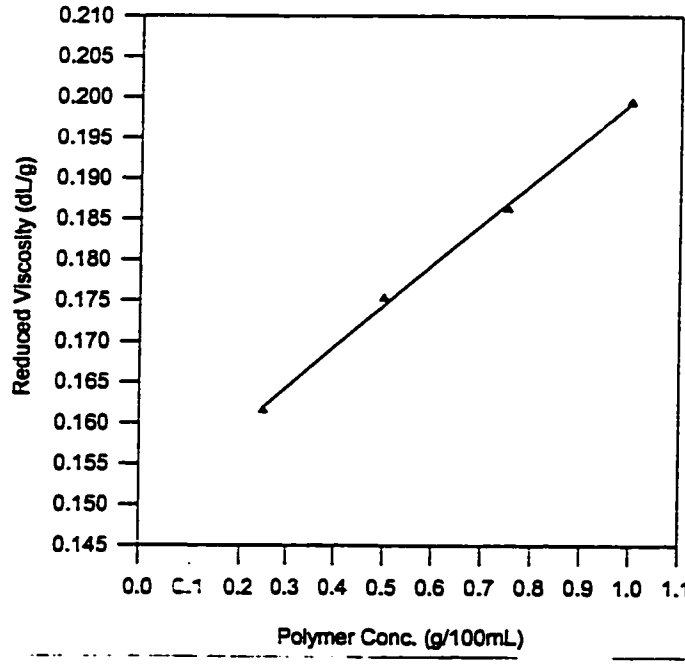



Figure 34 Viscosity behavior of zwitterionic polyelectrolyte **(9)** (Entry 2,Table 5) in 1.0N NaCl solution at 30°C

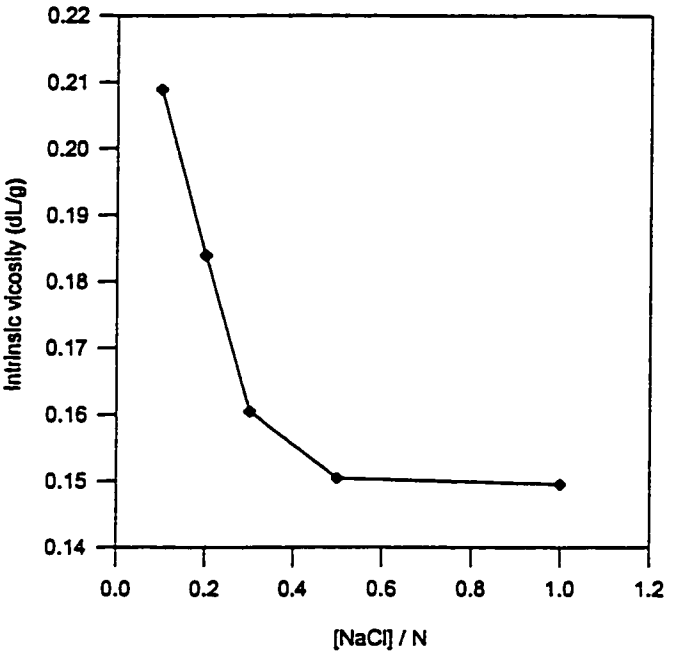
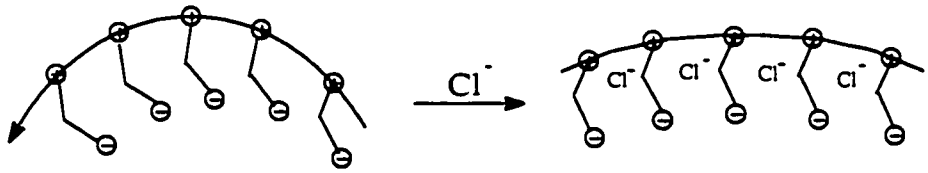



Figure 35 Variation of intrinsic viscosity of zwitterionic polyelectrolyte **(9)** (Entry 2,Table 5) with NaCl concentration at 30°C

that the zwitterionic polymer **(9)** exhibits polyelectrolytic viscosity behavior. A comparison of the viscosity of zwitterionic polymer **(9)** in 0.1N NaCl (Figure 30) with that of the polyelectrolyte **(8)** reveals that there is an enhancement in the intrinsic viscosity. This enhancement is explained as resulting from the presence of zwitterionic moiety in polymer **(9)**. Polyampholytes are known to exhibit increased intrinsic viscosity in solution of strong electrolytes such as NaCl. This is because in the absence of the added electrolyte the pendent groups that bear the zwitterions tend to coil due to electrostatic attractive forces between the opposite charges on the zwitterionic portion of the molecule. Addition of electrolyte partially neutralizes the charge on the polymer chain. With quaternary amine polyampholytes, the positive charge on the polymer backbone is neutralized efficiently by the anion from added electrolyte (e.g., $Cl^-$ from NaCl). The positive ion ($Na^+$ in NaCl) is less effective in neutralizing the negative end of the zwitterion. Mutual repulsion between negative charges on neighboring pendent groups drives the polymer chains to adopt a more open rod-like structure with consequent rise in hydrodynamic volume as shown in Scheme 4.




**Scheme 10**

The poor ability of the cation (e.g., $Na^+$) to neutralize the anionic portion of the pendent group is attributed to the fairly large hydration shell of this cation in water, which prevents the cation from approaching the negative charge on the polymer pendent group

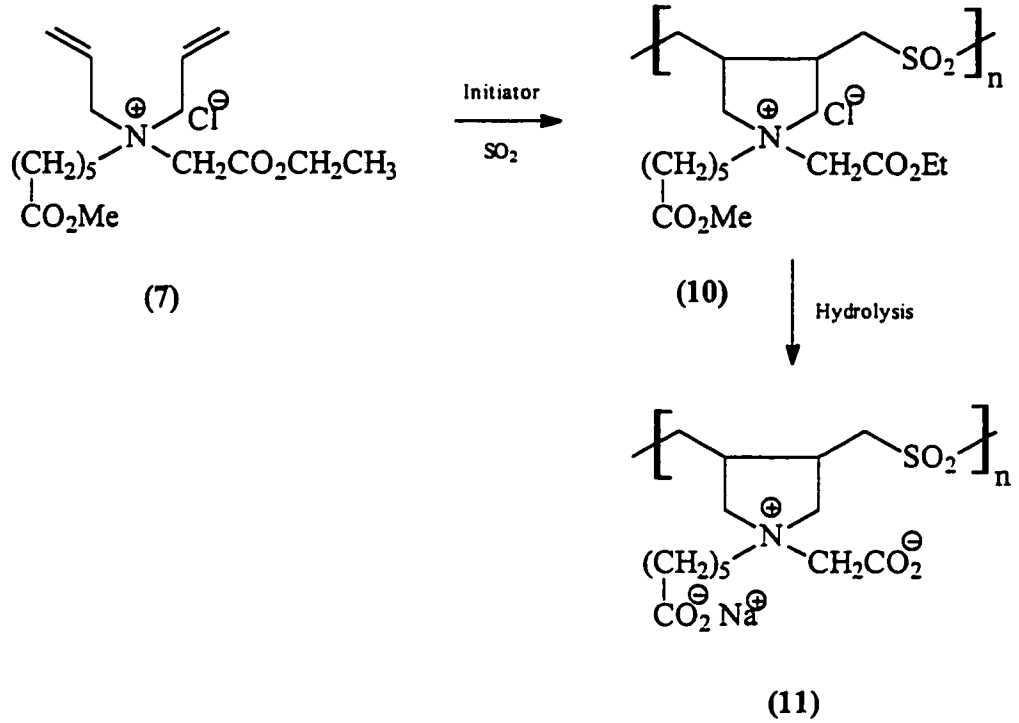
closely enough to effectively neutralize it. This phenomenon is referred to as antipolyelectrolyte effect.

The net effect of the addition of strong electrolyte is therefore an increase in hydrodynamic volume and consequent rise in intrinsic viscosity of polyampholytes.

It is interesting that although the overall viscosity behavior of **(9)** is that of a polyelectrolyte, the antipolyelectrolyte effect expected from the zwitterion pendent group has manifested itself in **(9)** having higher intrinsic viscosity in NaCl solution relative to **(8)**.

## 3.4 Copolymerization of the monomer (7) with $SO_2$

Copolymers of the quaternary ammonium salts with $SO_2$ (a class of polysulfones) have been used as flocculent, adhesives, thickeners and in paints.




(7) (10) (11)

**Scheme 11**

As shown in Scheme 11, monomer (7) was copolymerized with $SO_2$ to yield polysulfone (10). The monomer (7) and $SO_2$ were dissolved dimethlysulfoxide (DMSO) and ammonium persulfate (APS) was used as initiator. Table 7 presents the result of the polymerization reactions. Maximum intrinsic viscosity in 0.1 N NaCl solution of 0.200 dl/g was obtained at 45°C using 25 mg APS/g of monomer (Entry 2, Table 7). For a given initiator concentration increase in reaction temperature resulted in improved yield but no significant change in intrinsic viscosity (compare Entry 2 and 3, Table 7).

**TABLE 7: Results of Copolymerization reaction[a].**

| Entry No. | APS mg/g monomer | Temp. (°C) | Yield[b] (%) | $\eta_{sp}/C$ (dL/g)[c] |
|---|---|---|---|---|
| 1 | 5.0 | 45 | 55 | 0.161 |
| 2 | 10 | 45 | 61 | 0.169 |
| 3 | 10 | 50 | 78 | 0.169 |
| 4 | 15 | 50 | 81 | 0.183 |
| 5 | 20 | 50 | 80 | 0.195 |
| 6 | 25 | 50 | 83 | 0.200 |

[a]Monomer (30 mmol), $SO_2$ (30 mmol), was polymerized in DMSO (5.8 g) for 20 h.
[b]Based on Monomer:$SO_2$=1:1 in copolymer.
[c]Viscosity of 1-0.125 % polymer solution on 0.1 N NaCl at 30 °C was measured in Ubbelohde Viscometer (K=0.005989).

The viscosity behavior of a polymer sample (Entry 5,Table 7) in the absence of NaCl is shown in Figure 36. The concave upward plot is characteristic of polyelectrolytes. The viscosity in 0.1 N NaCl solution of polymer samples (Entries 1,2,3 and 5, Table 7) prepared using different initiator concentrations is given in Figures 37, 38,39 and 40.

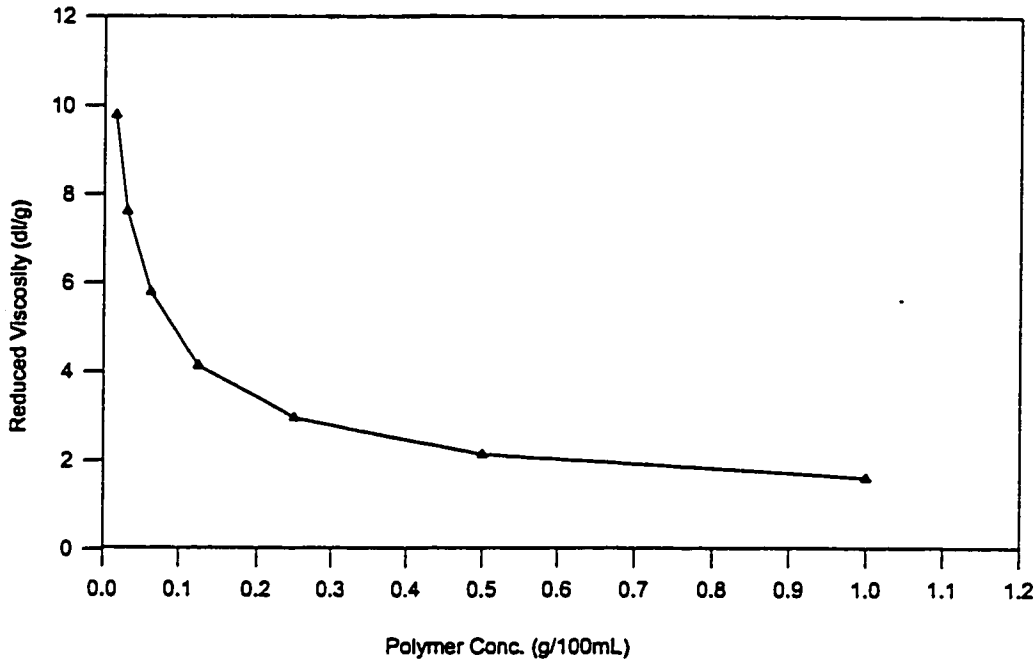



Figure 36 Viscosity behavior of copolymer polyelectrolyte **(10)** (Entry 5,Table 7) in deionized water at 30°C

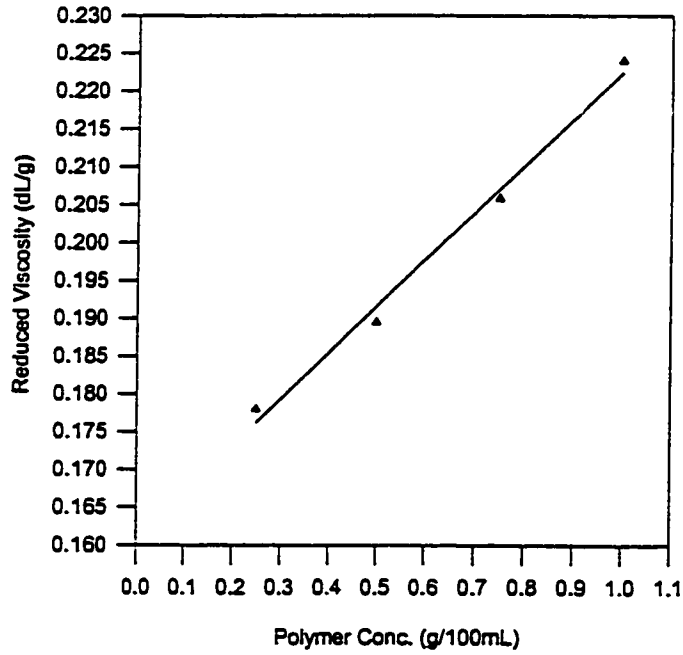



Figure 37 Viscosity behavior of copolymer polyelectrolyte **(10)** (Entry 1,Table 7) in 0.10 N NaCl solution at 30°C

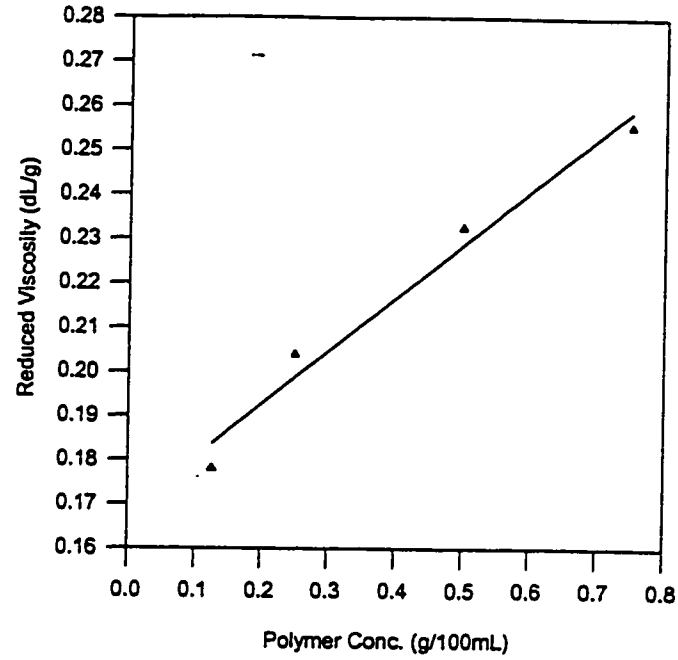



Figure 38 Viscosity behavior of copolymer polyelectrolyte **(10)** (Entry 2,Table 7) in 0.10 N NaCl solution at 30°C

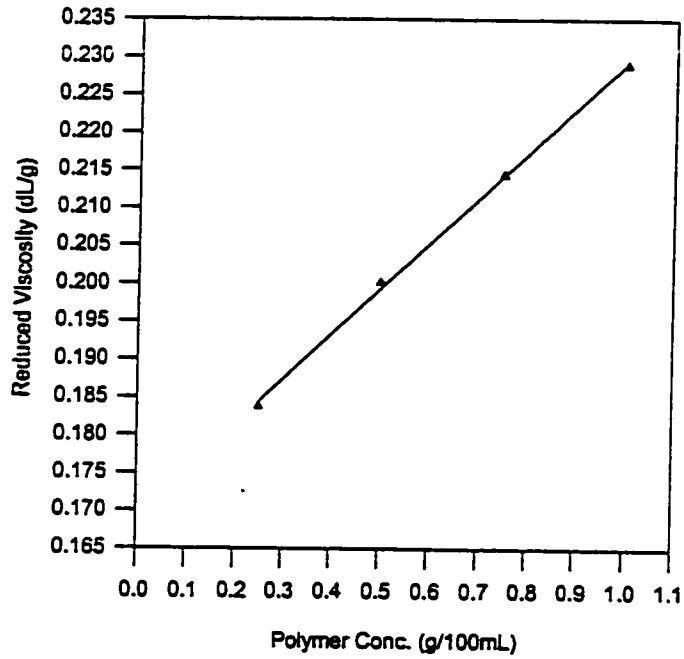



Figure 39 Viscosity behavior of copolymer polyelectrolyte **(10)** (Entry 3,Table 7) in 0.10 N NaCl solution at 30°C

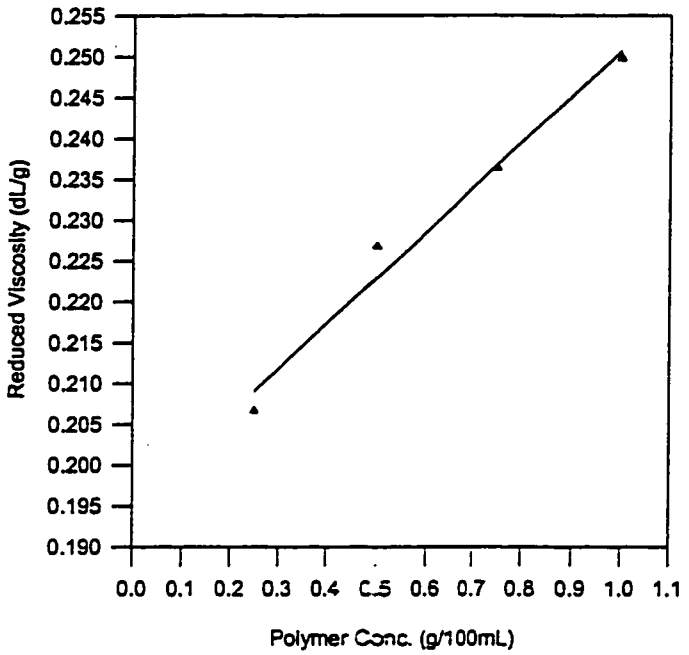



Figure 40 Viscosity behavior of copolymer polyelectrolyte **(10)** (Entry 5,Table 7) in 0.10 N NaCl solution at 30°C

The polysulfone was found to be soluble in water and methanol but only sparingly soluble in acetone. The pH of 1% solution of copolymer **(8)** was found to be 3.11. The polymer decomposes at 184°C turning yellow and chars at 237°C. The thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) is shown in Figure 41.

The FTIR spectrum of the polysulfone is shown in Figure 42. The two strong bands at 1312 $cm^{-1}$ and 1126 $cm^{-1}$ were assigned to the symmetric and antisymmetric vibrations of $SO_2$. The presence of ester carbonyl groups is indicated by the absorption at 1738 $cm^{-1}$. The strong band at 3439 $cm^{-1}$ shows the hygroscopic nature of the copolymer. The $^1H$ NMR and $^{13}C$ NMR of copolymer **(10)** are shown in Figure 43 and 44 and confirm the assigned structure of the copolymer. Comparison of Figure 43 with the $^1H$ NMR spectrum of homopolymer (Figure 14) reveals a downfield shift (from the region of δ 2.75 –0.70 to δ 4.75 – 3.00) of the chemical shift for the protons labeled "a" due to the presence of the electronegative $SO_2$ moiety in the polymeric backbone. As is the $^{13}C$ NMR of the homopolymer the two carbonyl functionality have signals at significantly different chemical shift values. This may be due to the difference in proximity of the two ester functionalities to the positively charged quaternary nitrogen in the conformation adopted by the polymer macromolecule.

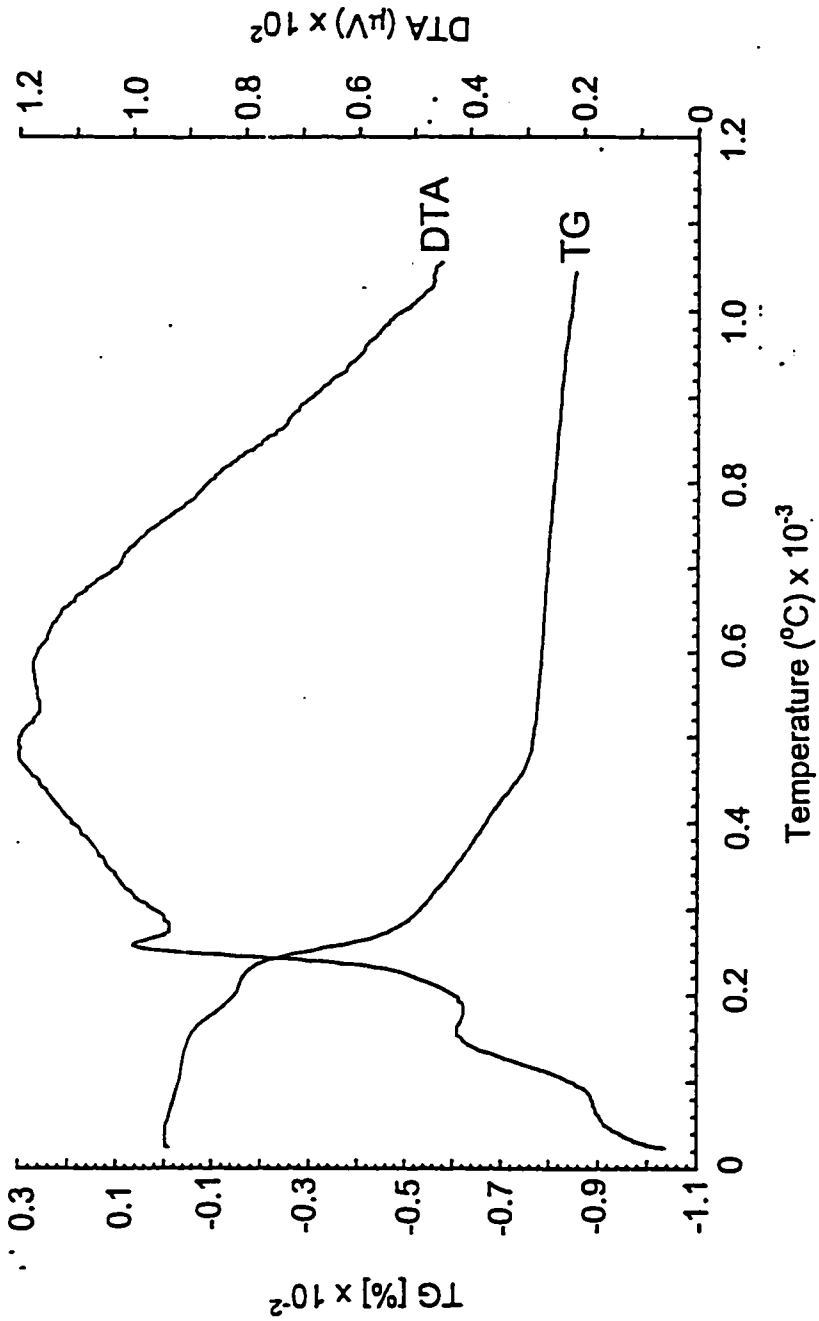



Figure 41 DTA/TG thermograms of polymer **(10)**

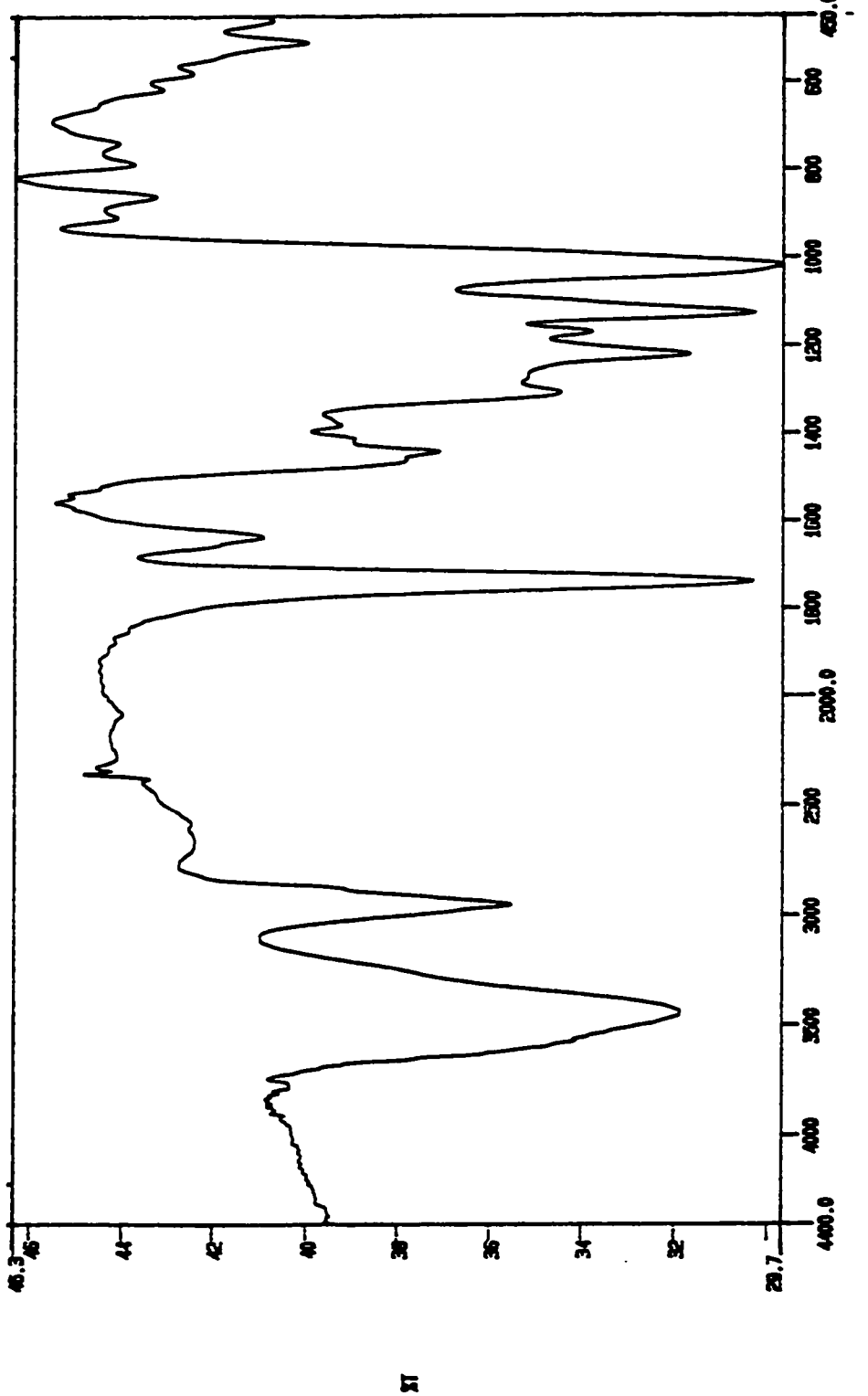



Figure 42 FTIR spectrum of polymer **(10)** in KBr at 20°C

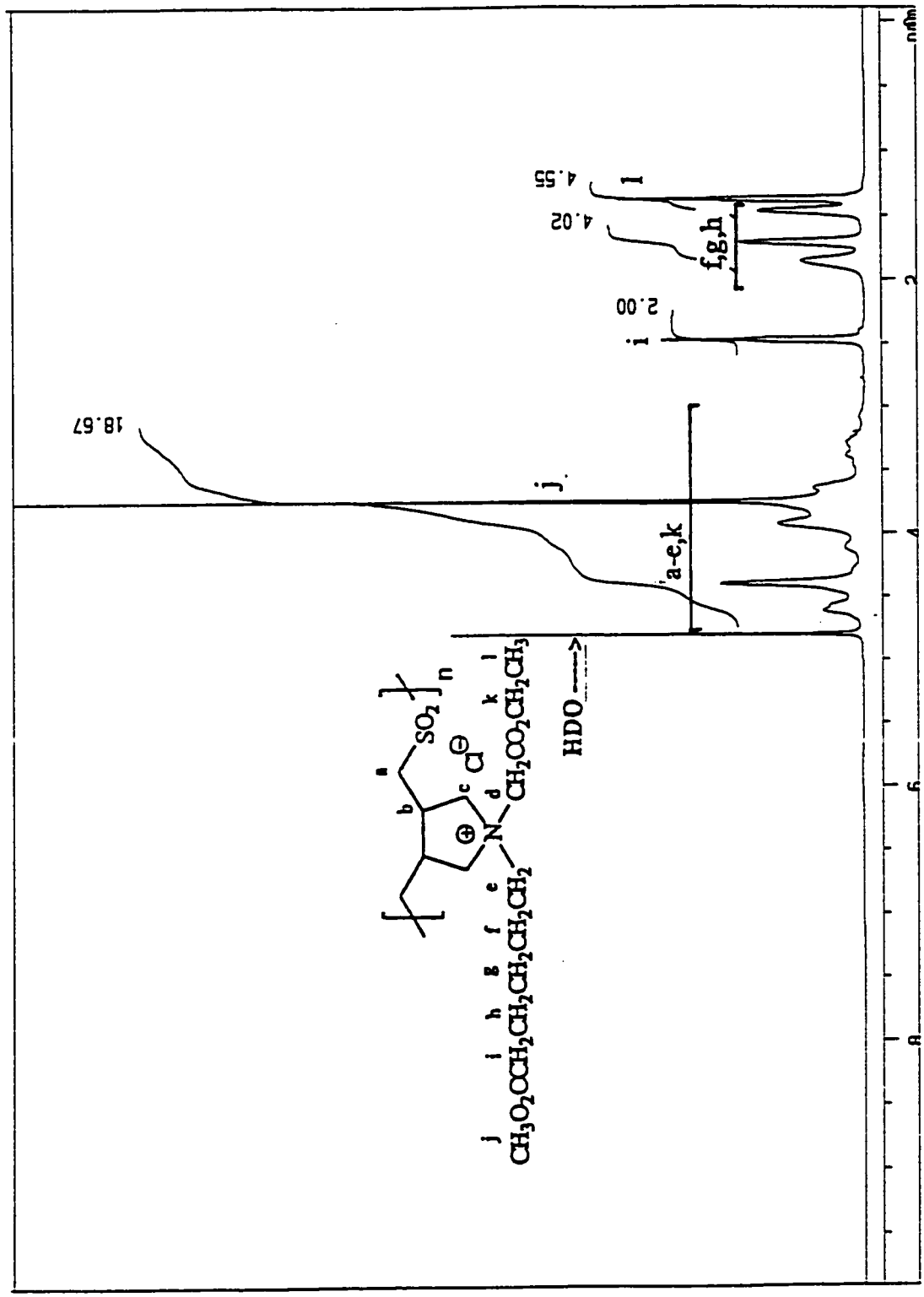



Figure 43 1H NMR spectrum of polymer (10) in $D_2O$ at 20°C

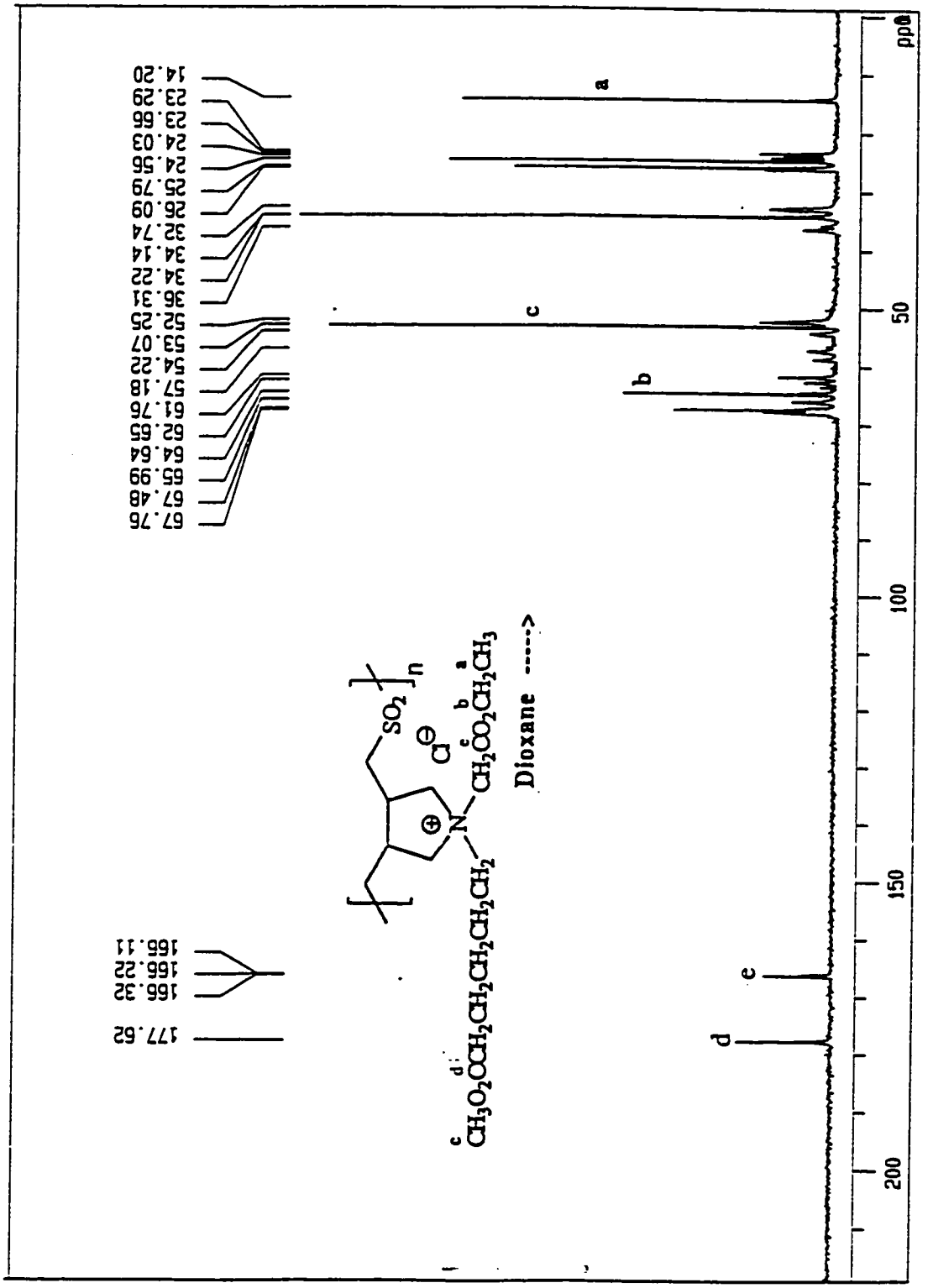
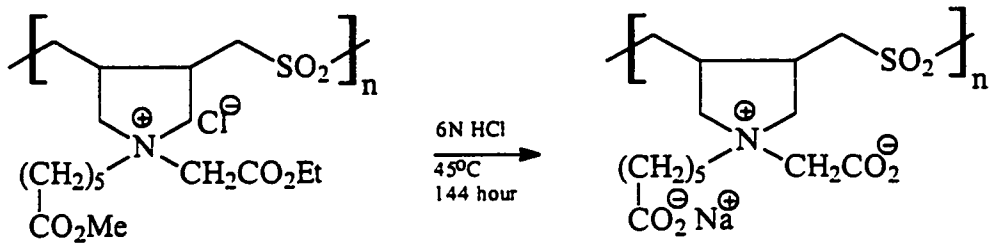



Figure 44 13C NMR spectrum of polymer (10) in $D_2O$ at 20°C

## 3.5 Hydrolysis of copolymer (10) to zwitterionic copolymer (11)

The copolymer **(10)** was hydrolyzed under acidic conditions to the zwitterionic polysulfone **(11)** with excellent yield.




**(10)** **(11)**

**Scheme 12**

The white copolymer decomposes between 225 and 230 °C, it turns brown above this temperature and finally chars at 263 °C. The DTA and TGA Thermograms are shown in Figure 45. The pH of 1% solution of copolymer **(11)** was found to be 9.79.

The results of the hydrolysis reaction are summarized in Table 8. The table includes intrinsic viscosity of several copolymer samples prior to and after hydrolysis.

The IR spectrum of **(11)** (Figure 46) shows no absorption for the ester functionalities. The strong bands at 1306 $cm^{-1}$ and 1128 $cm^{-1}$ indicate the presence of the $SO_2$ moiety. Also, the $^1H$ NMR and $^{13}C$ NMR spectra (Figures 47 and 48) confirm that complete hydrolysis has been achieved. The signals for the methoxy and ethoxy protons are absent in the $^1H$ NMR spectrum. The $^{13}C$ NMR showed no signals for the $OCH_3$ and $OCH_2CH_3$ carbons.

**TABLE 8: Results of hydrolysis reaction[a].**

| Entry No. | Yield (%) | $\eta_{sp}/C^{b}$ (dL/g) ZEP[c] | $\eta_{sp}/C^{b}$ (dL/g) PE[d] |
|---|---|---|---|
| 1 | 87 | 0.405 | 0.169 |
| 2 | 93 | 0.470 | 0.161 |
| 3 | 84 | 0.580 | 0.195 |
| 4 | 95 | 0.592 | 0.200 |
| 5 | 98 | 0.445 | 0.169 |

[a]5g polysulfone / 100mL 6N HCl was stirred at 45 °C for 6 days in all hydrolysis reactions.
[b]Viscosity of 1-0.125% polymer solution in 0.1N NaCl at 30°C was measured in Ubbelohde Viscometer, K=0.005989.
[c]ZEP:Zwitterionic polyelectrolyte (11).
[d]PE: Corresponding polyelectrolyte (10).

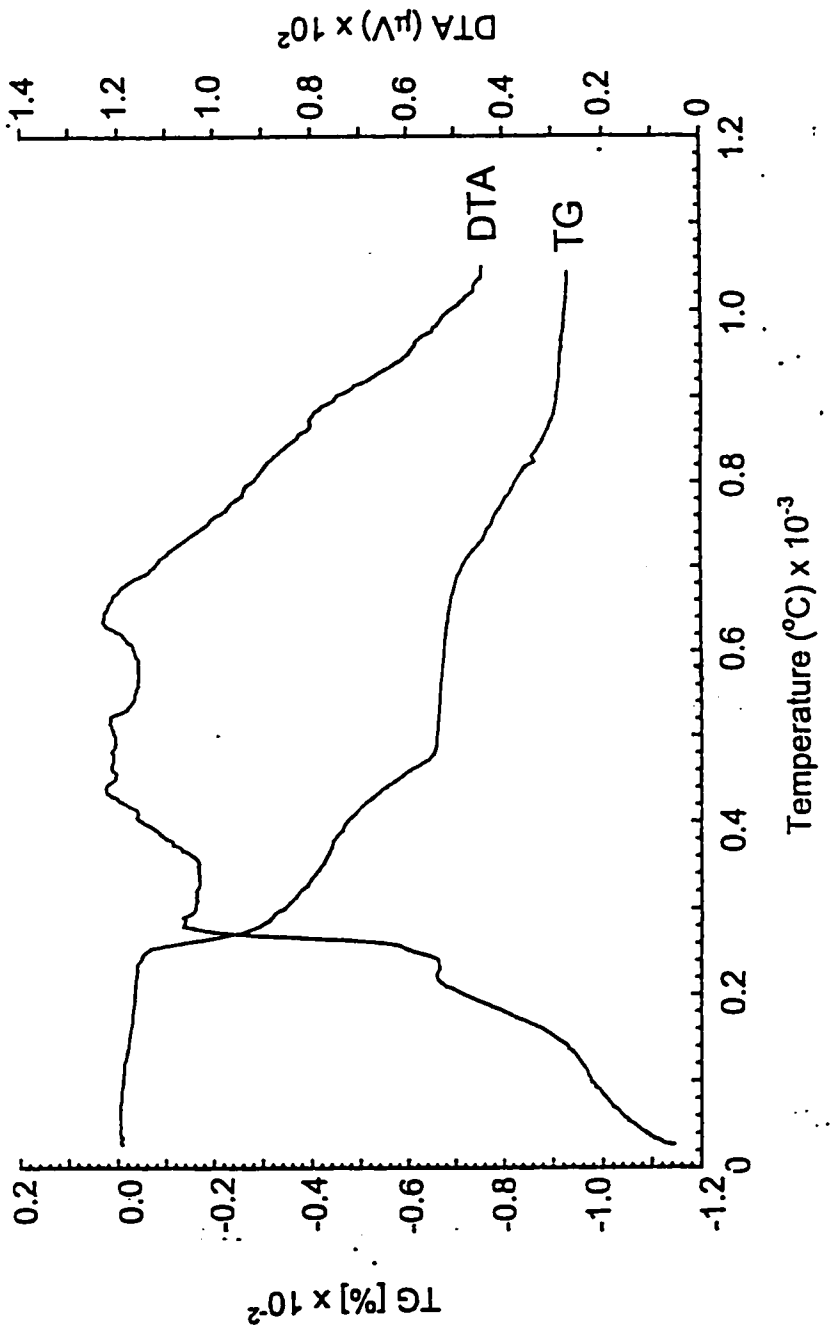



Figure 45 DTA/TG thermograms of polymer **(11)**

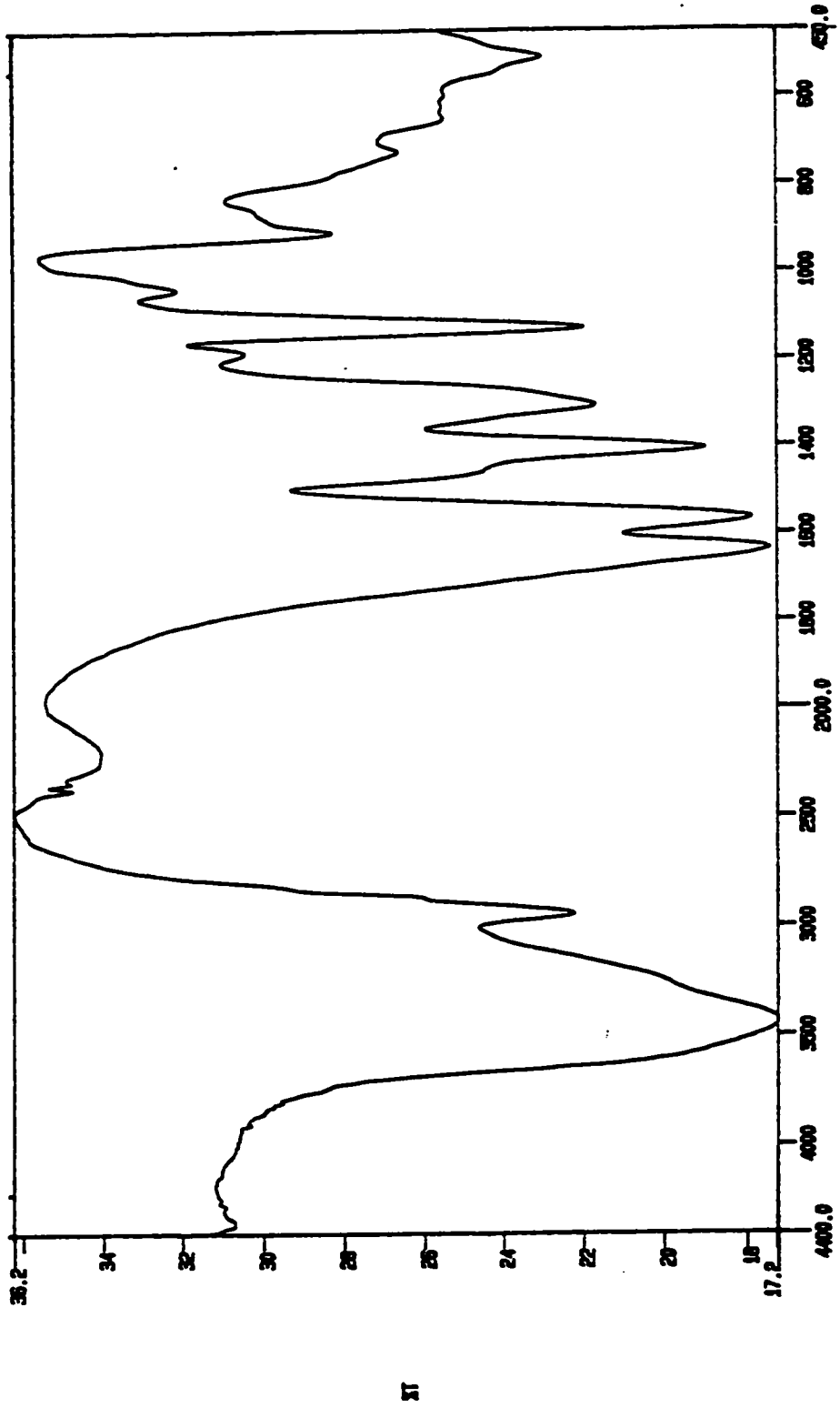



Figure 46 FTIR spectrum of polymer **(11)** in KBr at 20°C

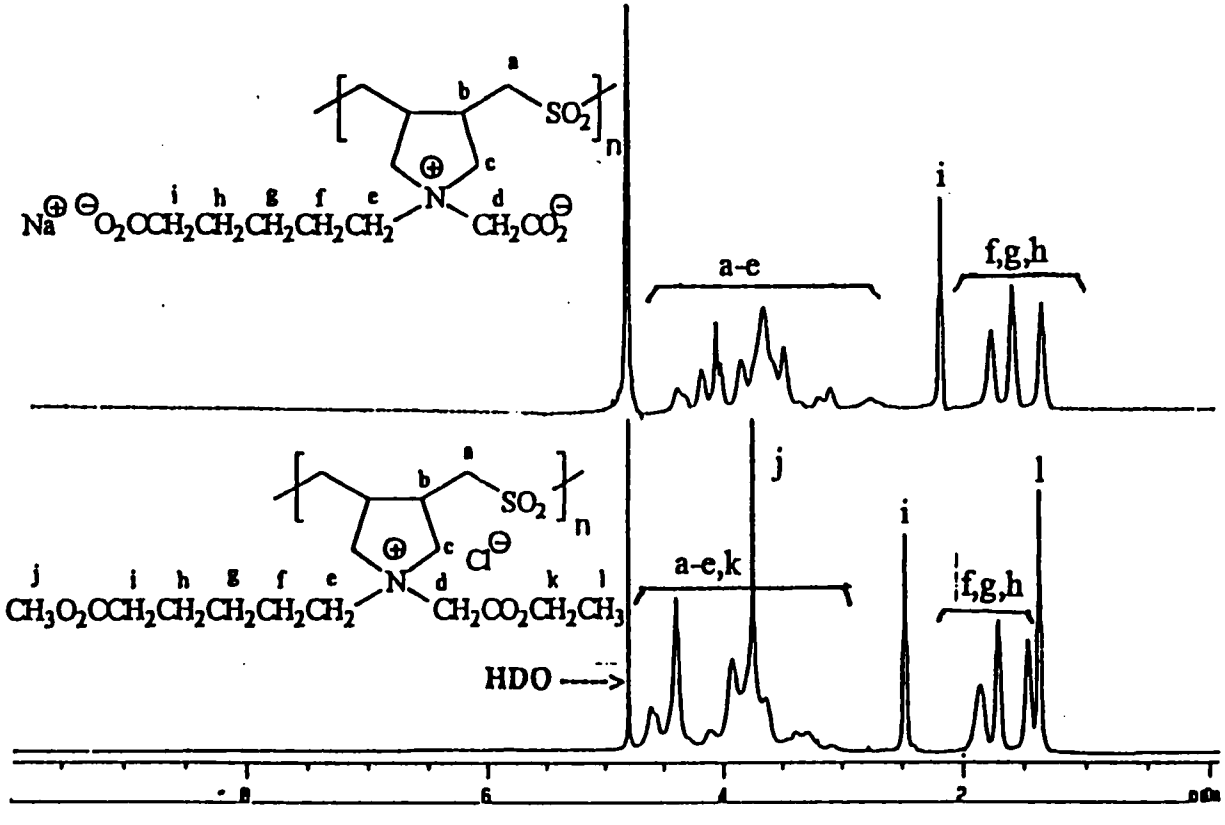



Figure 47 1H NMR spectra of Polymer **(10)** and **(11)** in $D_2O$ at 20°C

(showing complete hydrolysis of the ester groups)

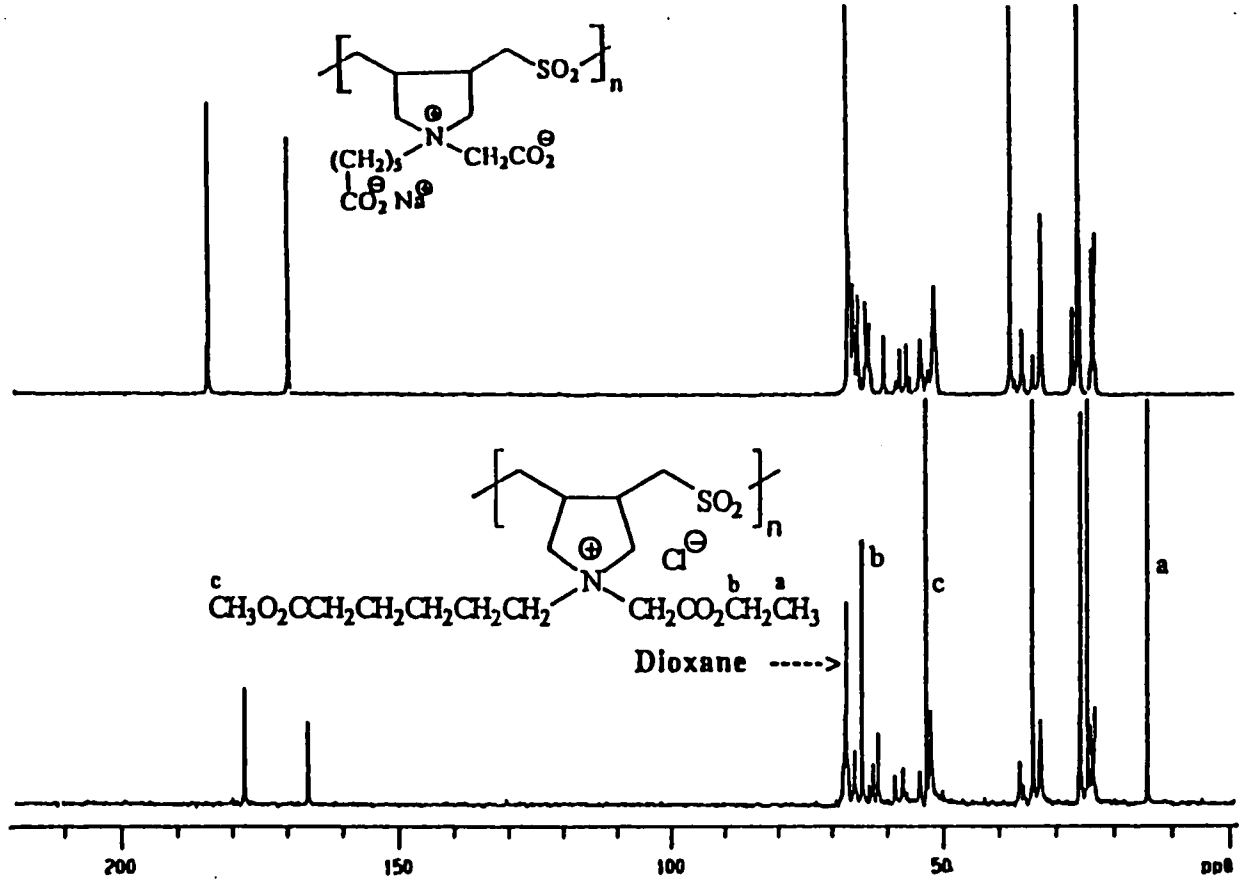



Figure 48 13C NMR spectra of Polymer **(10)** and **(11)** in $D_2O$ at 20°C (showing complete hydrolysis of the ester groups)

The viscosity behavior of the zwitterionic copolymer (Entry 4, Table 8) was studied in deionized water. The concave upward plot (Figure 49) is characteristic of polyelectrolytes. The intrinsic viscosity in 0.10 N NaCl of the polymer samples (Entries 1,2,3,4 and 5, Table 8) before and after hydrolysis is also included in Table 8. Intrinsic viscosity in 0.10 N NaCl was determined to confirm an increase relative to the unhydrolysed copolymer **(10)**. As is evident from the data in Table 8, there is more than a two fold increase in intrinsic viscosity upon hydrolysis of polyelectrolyte **(10)** to zwitterionic polysulfone **(11)**. For polymer sample (Entry 3, Table 8), the intrinsic viscosity of unhydrolyzed copolymer is 0.276 dL/g, while after hydrolysis to the zwitterionic polysulfone it exhibits an intrinsic viscosity of 0.580 dL/g. As in the homopolymers the increase is due to the presence of the zwitterionic moiety which imparts antipolyelectrolyte behavior to copolymer **(11)**.

The viscosity of a zwitterionic copolymer **(11)** sample (Entry 4, Table 8) was determined in different NaCl concentration. The viscosity data and Huggin's constant k', determined using Huggin's Equation are presented in Table 9 and Figure 50.

$$\eta_{sp/C} = [\eta] + k'[\eta]^2 C \qquad \text{(Huggin's Equation)}$$

Solubility of the copolymer **(10)** and zwitterionic copolymer **(11)** is shown in Table 10.

**TABLE 9: Intrinsic viscosity versus [NaCl] and Huggins' parameter**

| [NaCl] (N) | Intrinsic Viscosity[a] (dL/g) | k' |
|---|---|---|
| 0.1 | 0.592 | 0.628 |
| 0.2 | 0.476 | 0.834 |
| 0.3 | 0.432 | 0.991 |
| 0.5 | 0.425 | 0.891 |
| 1.0 | 0.418 | 0.681 |
| 1.5 | 0.411 | 0.699 |

[a]Viscosity of 1-0.125% polymer solution at 30°C was measured in Ubbelohde Viscometer (K=0.005989)

**TABLE 10: Solubility[a,b] of copolymer (10) and zwitterionic copolymer (11).**

| Solvent | ε | (10) | (11) |
|---|---|---|---|
| Water | 78.4 | + | + |
| Methanol | 32.7 | + | + |
| Formic acid | 58.5 | + | + |
| Formamide | 111.0 | + | + |
| Ethylene glycol | 37.3 | + | + |
| Triethylene glycol | 23.7 | + | + |
| Acetic acid | 6.15 | + | – |

[a]2% (w/w) of polymer solution was made after the mixture was maintained at 70°C for 1 hour and then the temperature lowered to 23°C.
[b]'+' indicates soluble; '-' indicates insoluble; '±' indicates partially soluble.

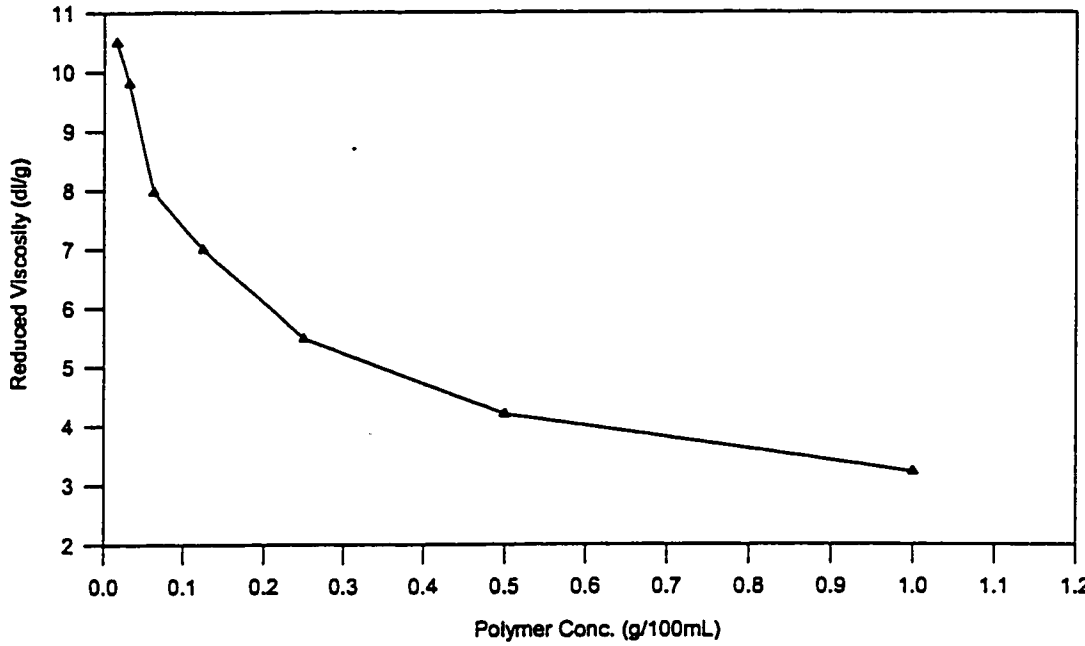



Figure 49 Viscosity behavior of zwitterionic copolymer **(11)** (Entry 4,Table 8) in deionized water at 30°C

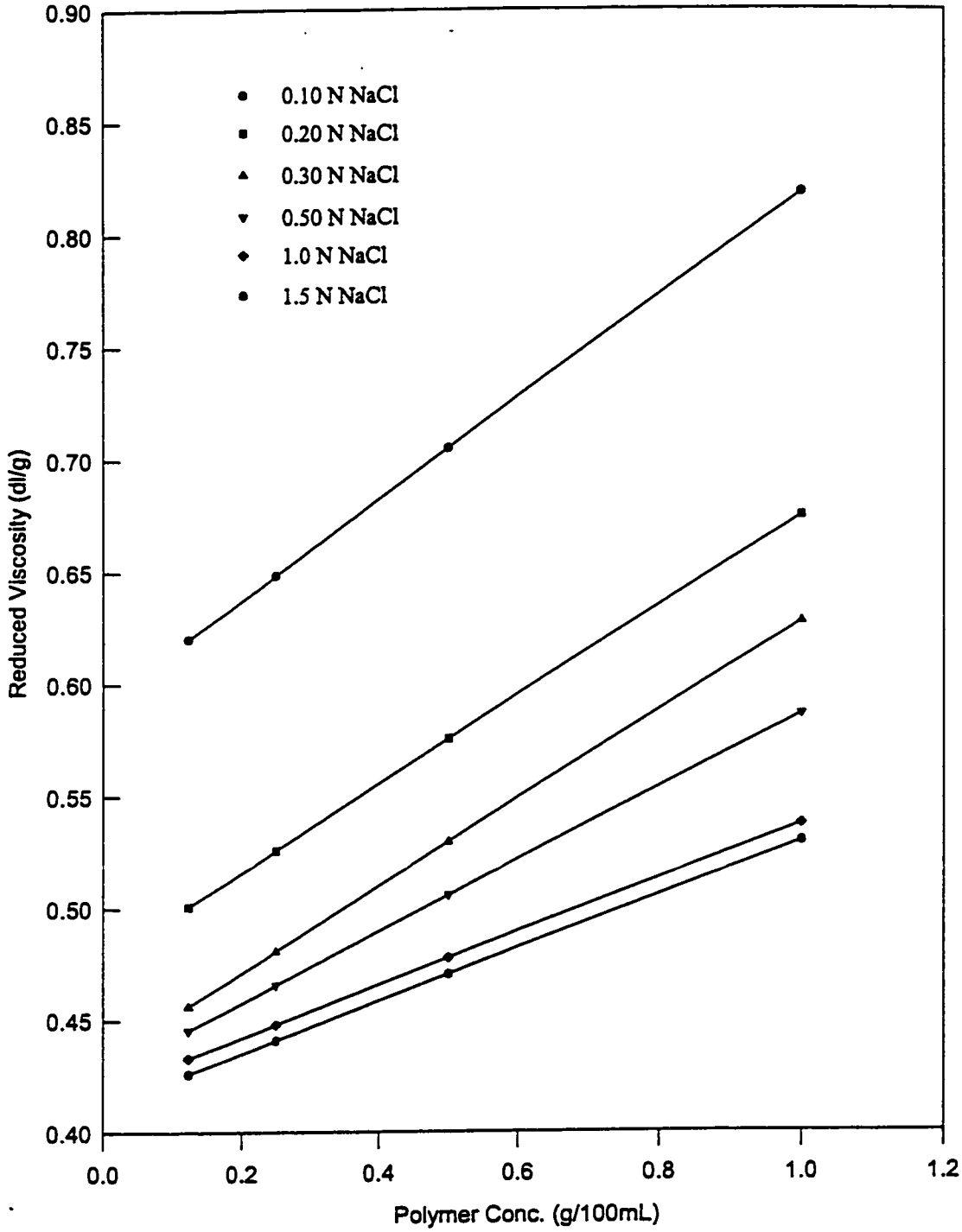
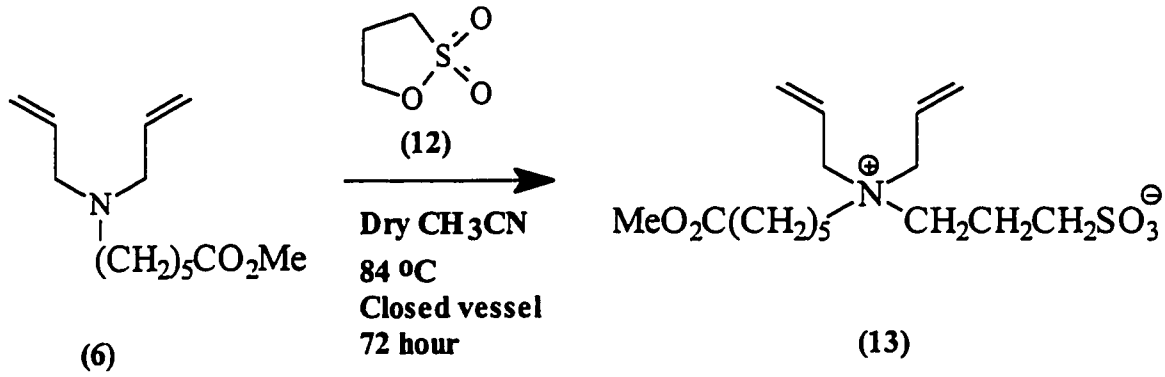



Figure 50 Viscosity behavior of zwitterionic copolymer **(11)** (Entry 4,Table 8) in 0.10, 0.20, 0.30, 0.50, and 1.0N NaCl solution at 30°C

## 3.6 Synthesis of zwitterionic monomer (13)

Zwitterionic monomer **(13)** was prepared by refluxing diallylamine **(6)** with 1 equivalent of propane sultone **(12)** in dry acetonitrile for 72 h. Monomer **(13)** was obtained in 70% yield.




**(6)** **(13)**

**Scheme 13**

The $^{1}H$ NMR, $^{13}C$ NMR, DEPT, COSY and CHSHF spectra of **(13)** are given in Figures 51, 52, 53, 54 and 55 respectively. These 1D and 2D NMR spectra confirm the assigned structure of monomer **(13)**.

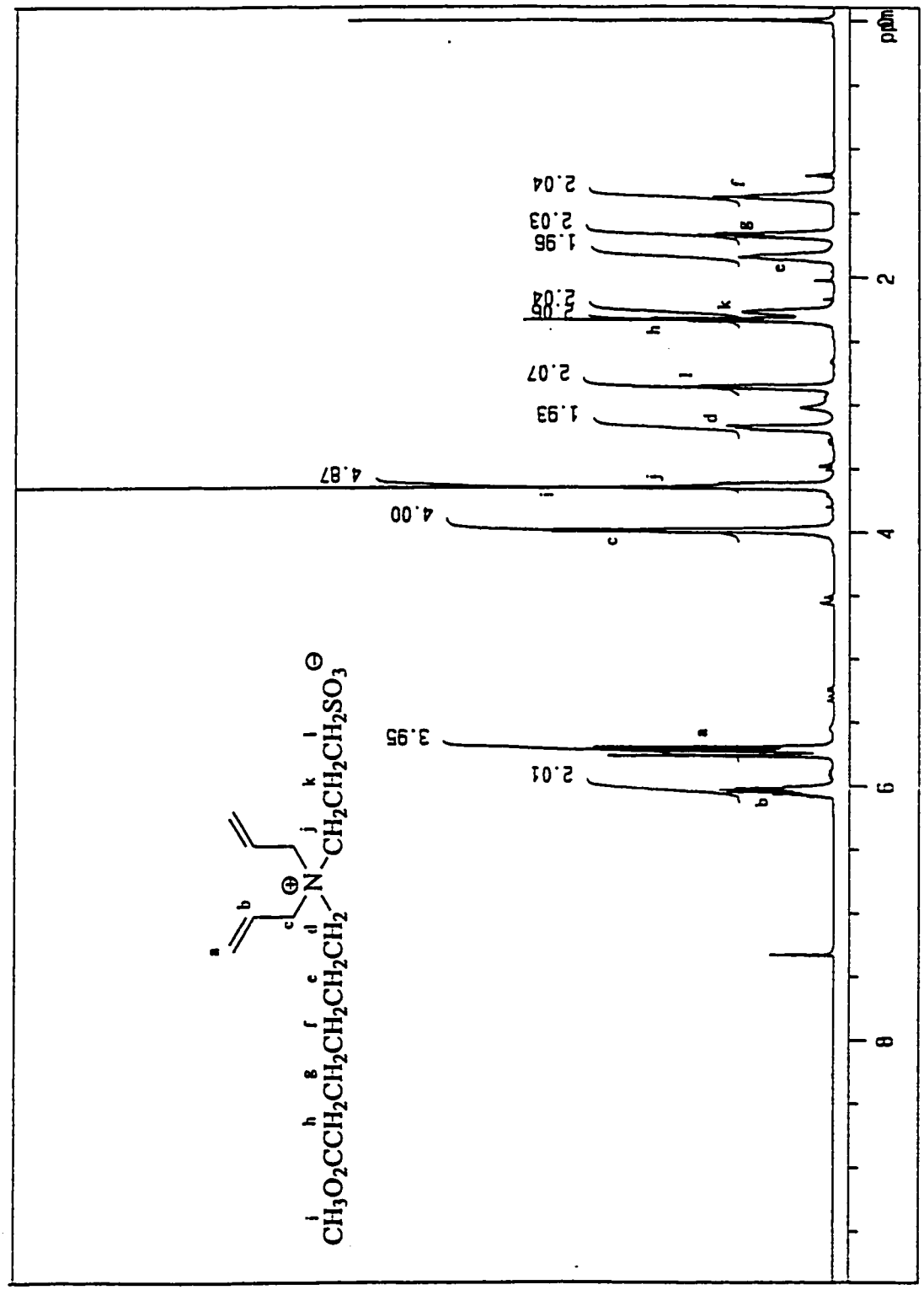



Figure 51 1H NMR spectrum of **(13)** in $CDCl_3$ at 20°C

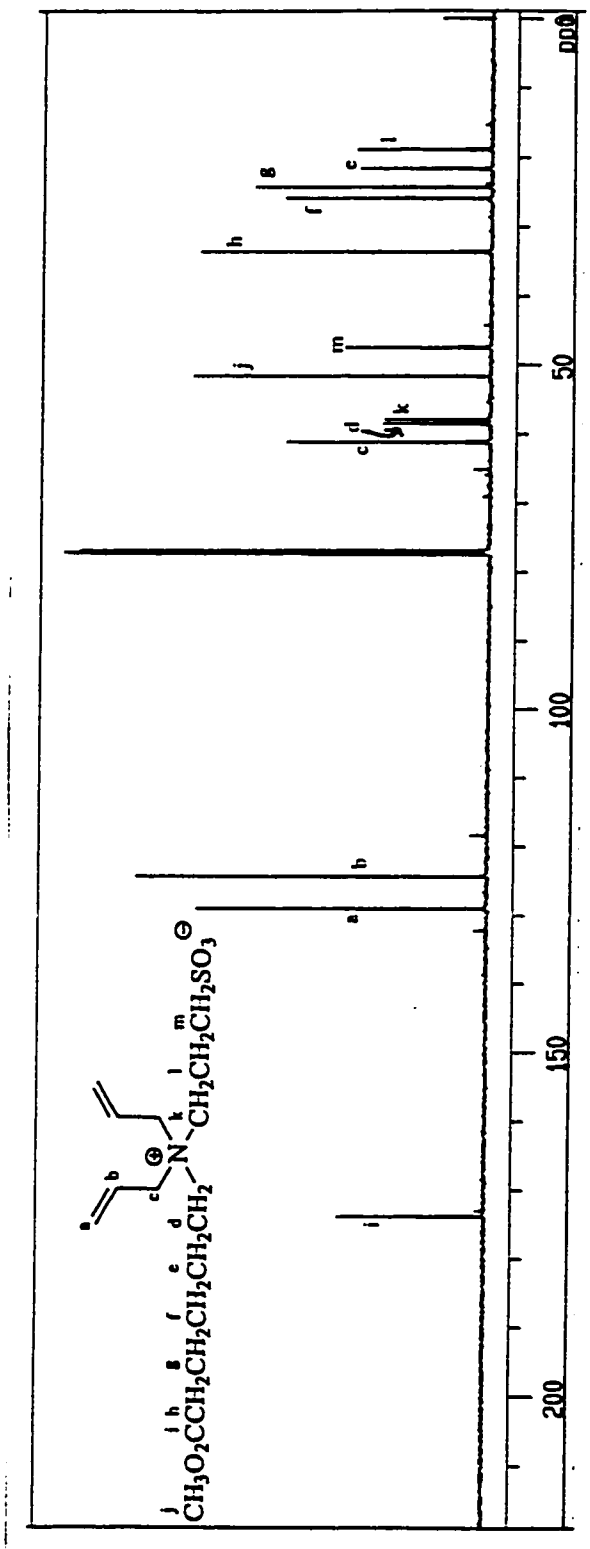



Figure 52 13C NMR spectrum of (13) in $CDCl_3$ at 20°C

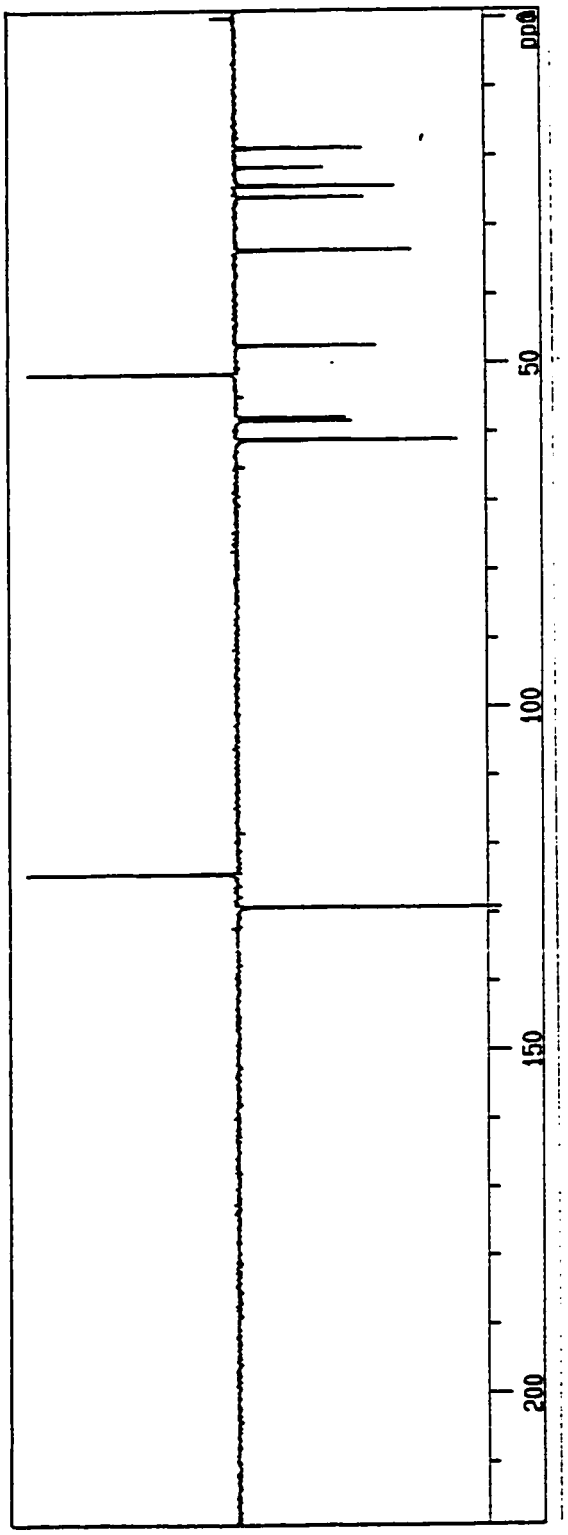



Figure 53 DEPT NMR spectrum of **(13)** in $CDCl_3$ at 20°C

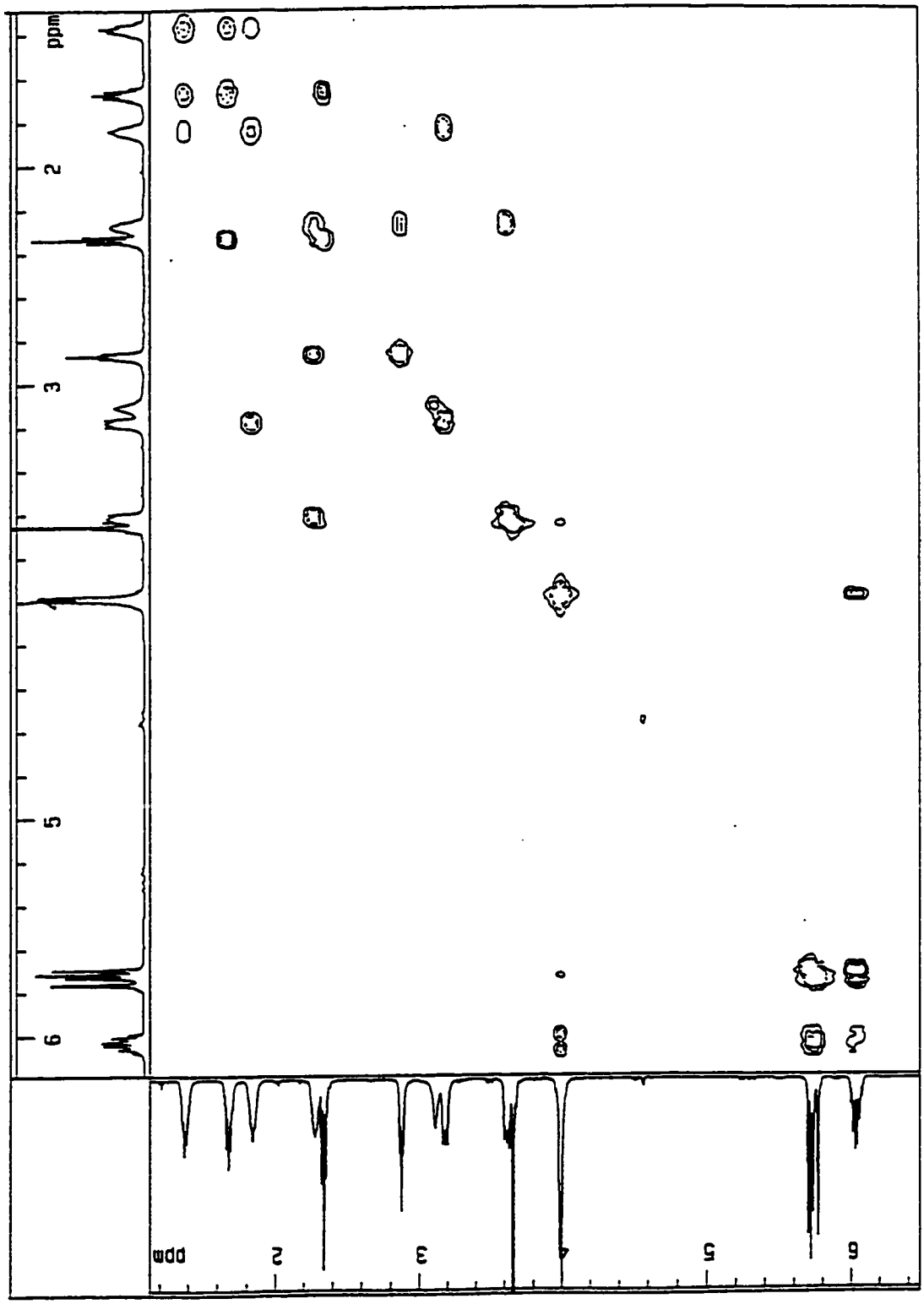



Figure 54 COSY 2D-NMR spectrum of **(13)** in $CDCl_3$ at 20°C

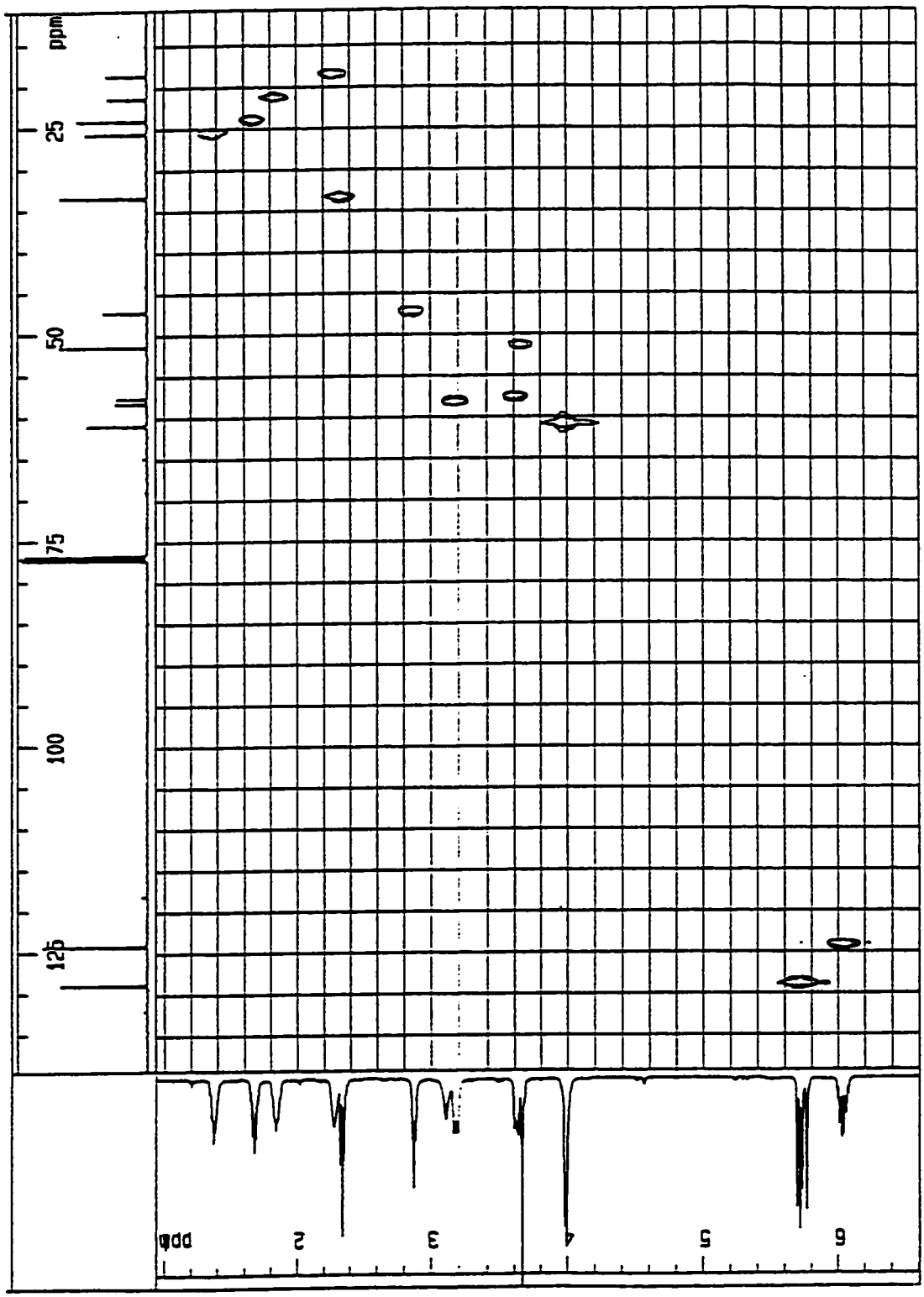
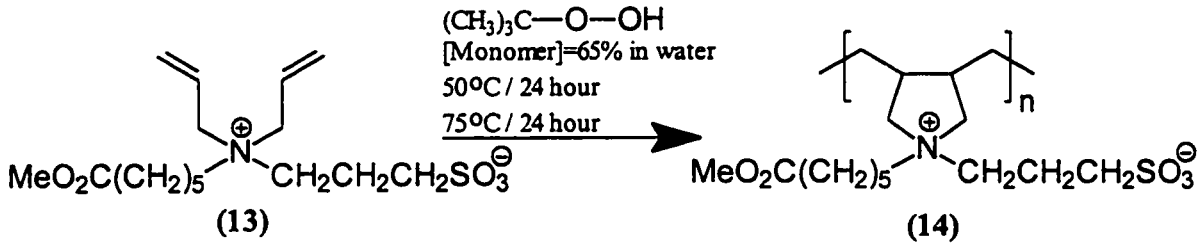



Figure 55 CHSHF 2D-NMR spectrum of **(13)** in $CDCl_3$ at 20°C

## 3.7 Synthesis and charactorization of polyampholyte (14)

Zwitterionic monomer (13) was polymerized to polyampholyte (14). The reaction was conducted in aqeuous medium using t-butyl hydroperoxide as initiator at 50°C for 24 h followed by a futher 24 h at 75 to 80 °C.




(13) (14)

**Scheme 14**

Figures 56 and 57 show the $^{1}H$ NMR and $^{13}C$ NMR spectra of polyampholyte (14). Absence of olefinic signals in both the $^{1}H$ and $^{13}C$ NMR spectra confirm that no residual unsaturation exists in polymer (14).

The solubility behavior of (14) was studied in water and dilute salt (NaCl) solution. As expected for all polybetaines, polymer (14) is insoluble in water but dissolves in dilute NaCl solution. This so called "antipolyelectrolyte effect" is explained in Scheme 15.

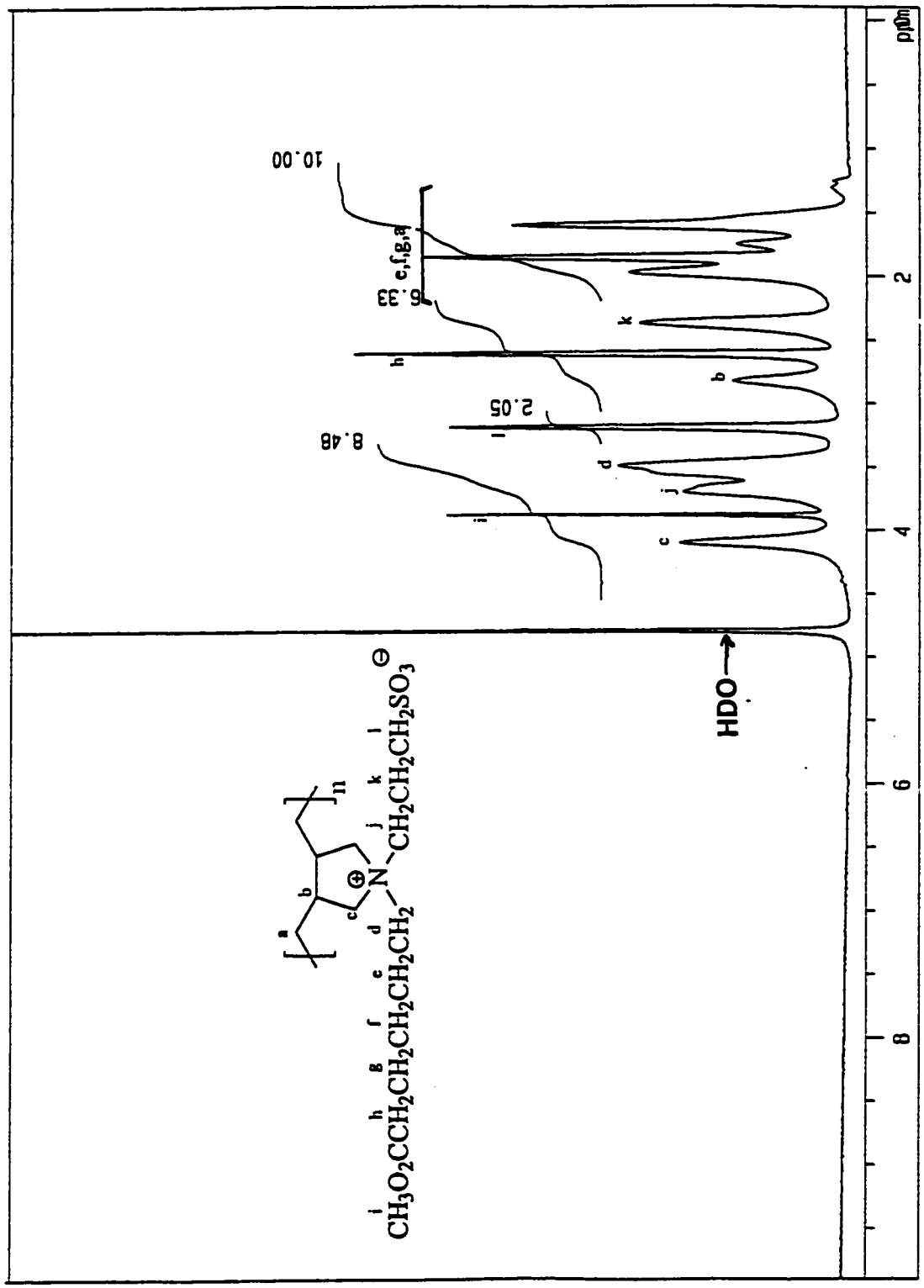



Figure 56 1H NMR spectrum of **(14)** in $D_2O$ at 20°C

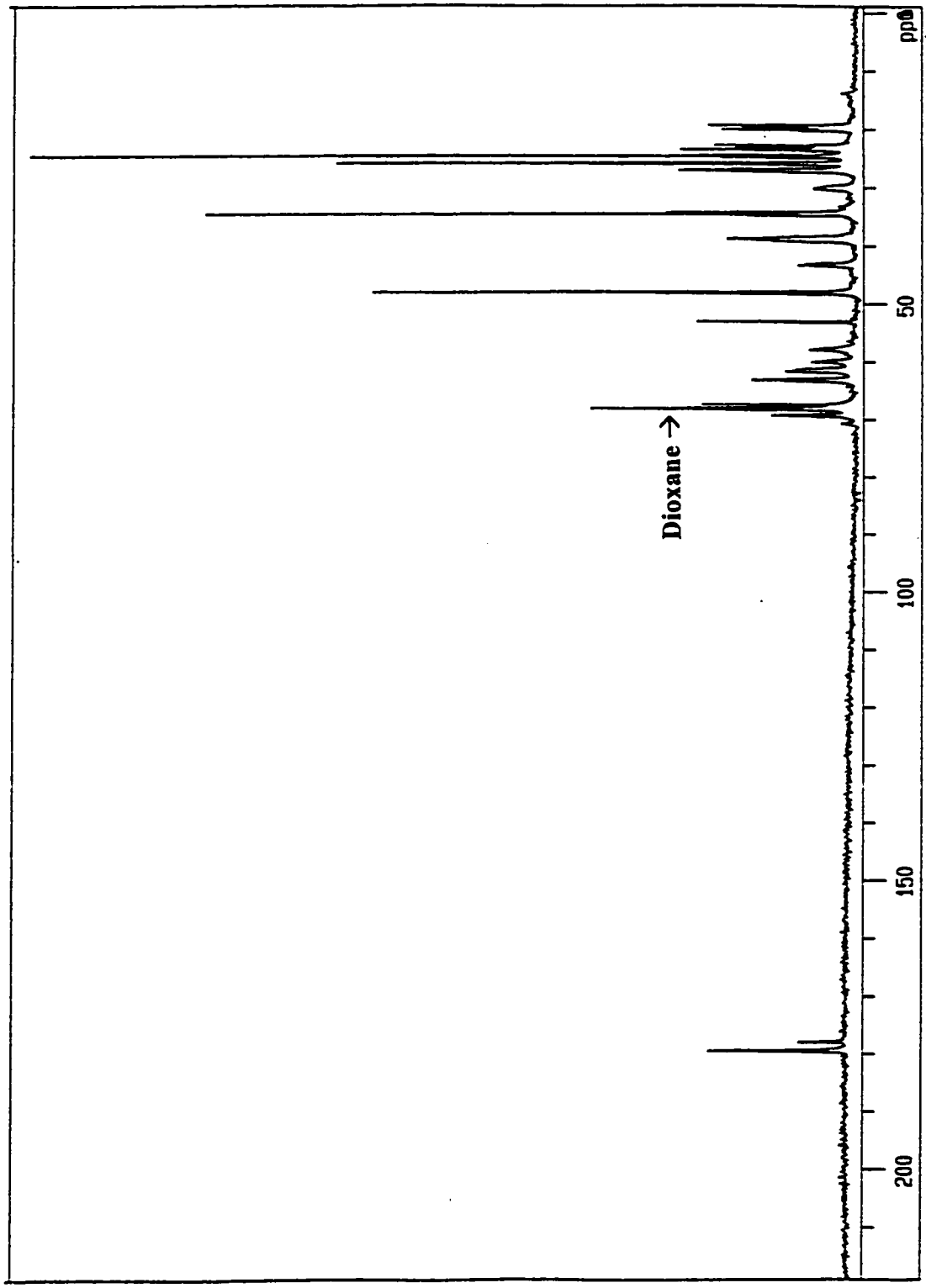
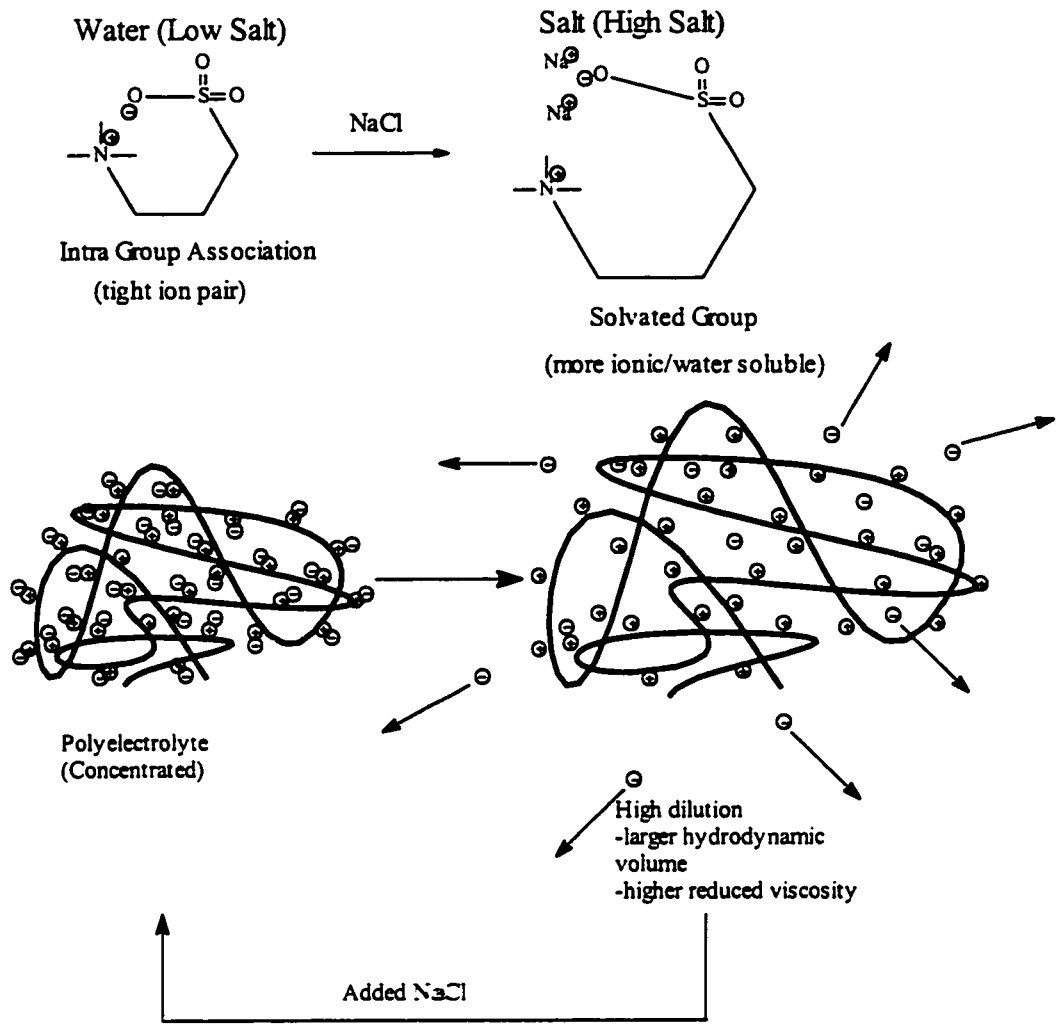



Figure 57 13C NMR spectrum of **(14)** in $D_2O$ at 20°C



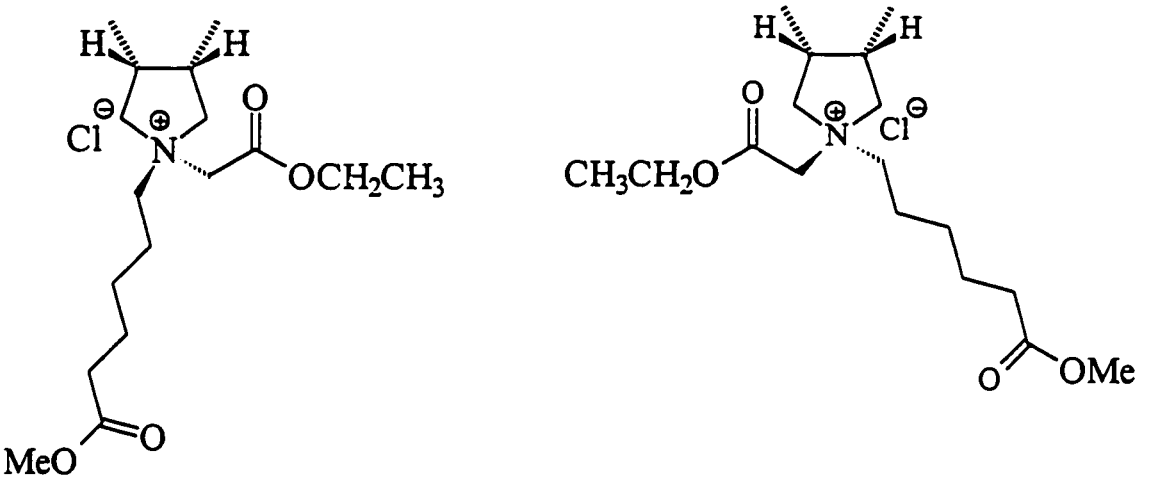

**Scheme 15**

As shown in Scheme 15, in water the polybetain molecules assume a collapsed conformation due to strong intrachain and intra-group associations resulting from electrostatic attactive forces between opposite charges of the zwitterionic moieties. These associations prevent the polybetain from dissolving in water. Upon addition of salt, however, these associations are disrupted and the macromolecule assumes an expanded conformation thereby going into solution.

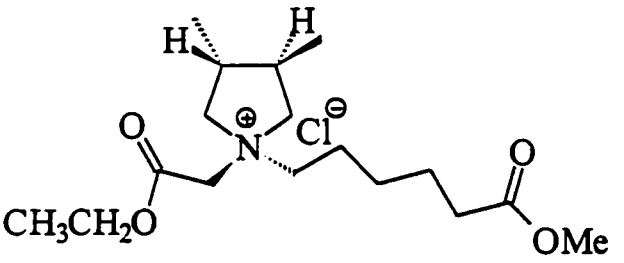
## 3.8 Geometric isomers of copolymer (10) from DEPT and 13C NMR spectra

The multiplicity of the carbonyl peaks in the $^{13}C$ NMR spectra of **(10)** suggested that the carbonyl carbons existed in more than one chemical environment. Theoretically, polymer **(10)** can occur as any of the three isomeric forms shown in Scheme 16.

**2-*Cis* forms**




**1-*Trans* form**




**Scheme 16**

Figure 58 shows the $^{13}$ C NMR spectrum of polymer **(10)**. The carbonyl peak around 166ppm (this is the carbonyl of the ethoxy ester group) is a triplet indicating that this carbonyl group is in three chemical environments. The more downfield carbonyl signal around 177 ppm consists of two apparent signals. The higher intensity of the upfield peak suggests that it results from two overlapping signals. It is proposed that this multiplicity of the carbonlyl signals in the $^{13}$ C NMR spectrum indicates that polymer **(10)** occurs in all three of the theoretically possible forms shown in Scheme 16. Our argument is further supported by the fact that the signals for C-2 and C-3 in the pyrollidine ring also shows similar splitting. The signals for these C-H carbons could be assigned unambiguously (around 32.5 ppm and 36.5 ppm) as they appear as positive peaks in the DEPT spectrum (Figure 59). The other two possible peaks at 13 ppm and 53 ppm being for the methyl carbons of the ethoxy and methoxy groups respectively.

Information from the $^{13}$C NMR and DEPT spectra therefore provides conclusive evidence for our proposal that polymer **(10)** occurs as a mixture of the three geometric forms shown in Scheme 16.

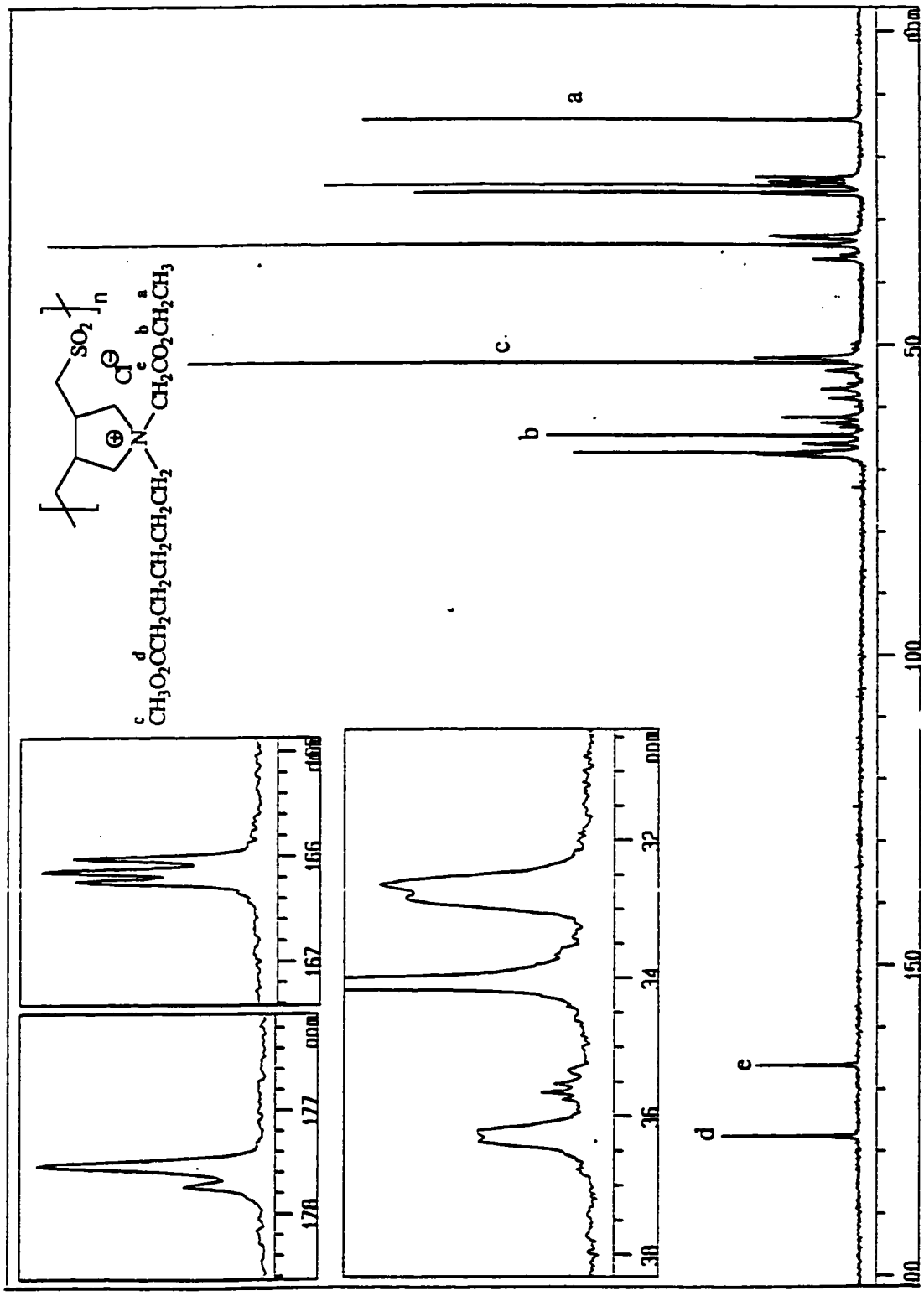



Figure 58 13C NMR spectrum of **(10)** in $D_2O$ at 20°C

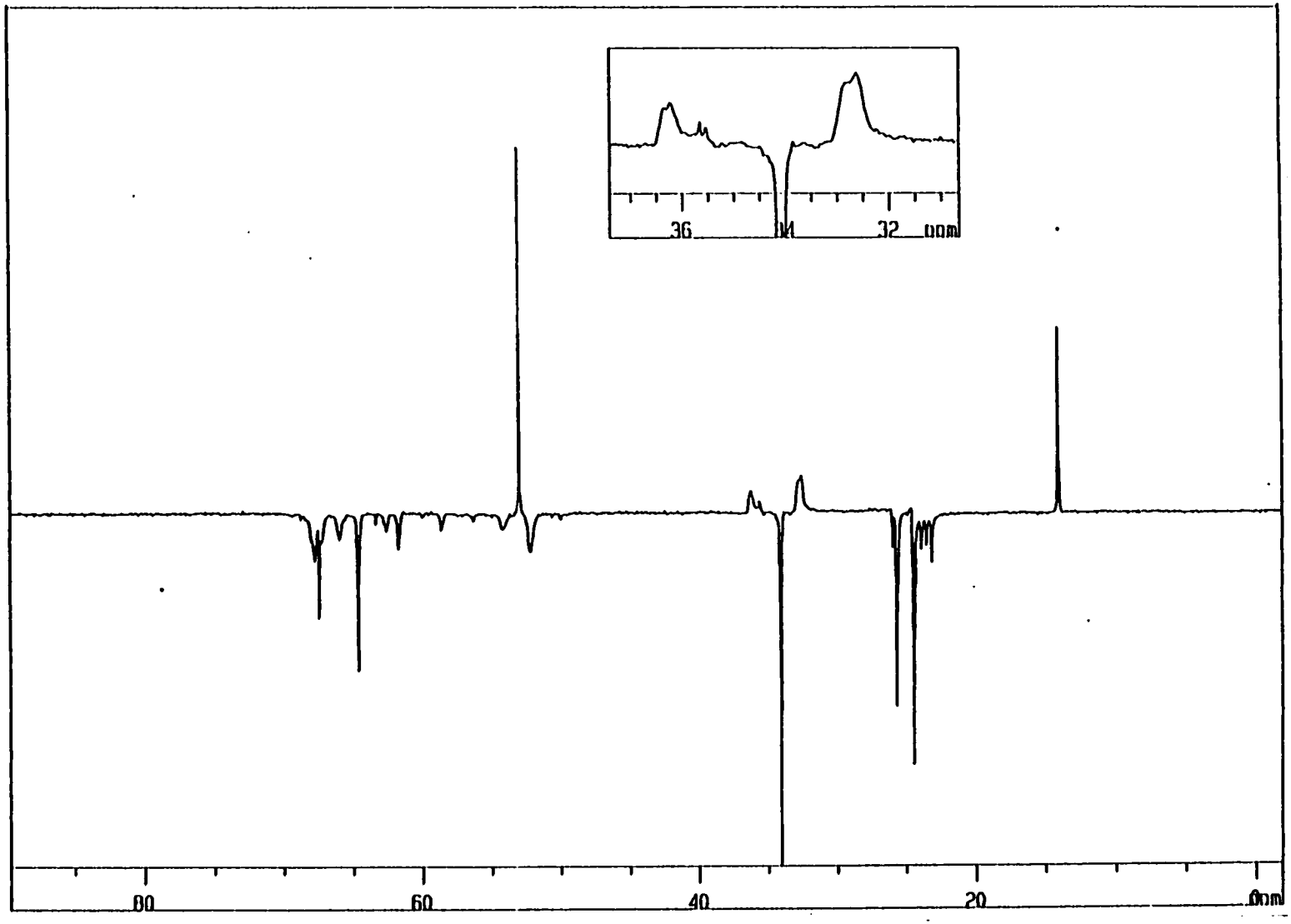



Figure 59 DEPT NMR spectrum of **(10)** in $D_2O$ at 20°C

# CHAPTER 4

# CONCLUSION

Zwitterionic polymers, known as polyampholytes and conventional polyelectrolytes have been used as thickeners and as such their solubility behavior in aqueous media and their dilute solution viscosity are of interest. Polyampholytes are insoluble in water but dissolve upon the addition of small quantities of strong electrolyte which increases the ionic strength of the solvent medium. Furthermore, polyampholytes exhibit enhanced viscosity upon increasing the ionic strength of the solution medium. In this work *N,N*-diallyl-*N*-(ethoxycarbonyl)methyl-*N*-(methoxycarbonyl)pentyl ammonium chloride (**7**) has been synthesized and its free radical polymerization and copolymerization with $SO_2$ have been accomplished. The resulting homopolymer (**8**) and copolymer (**10**) have been hydrolyzed to yield zwitterionic polymers (**9**) and (**11**). The structure of zwitterionic polymers (**9**) and (**11**) incorporates a zwitterionic moiety as well as an electrolytic ion pair. To the best of our knowledge, polymers possessing this special structural feature have not been synthesized to date. It has been shown in this study that such polymers exhibit unique solution properties. Zwitterionic polymers (**9**) and (**11**) are soluble in pure water unlike conventional polyampholytes. They exhibit higher salt tolerance than the corresponding polyelectrolytes (**8**) and (**10**) as indicated by their higher intrinsic viscosity in salt

solutions. However their viscosity behavior is characteristic of polyelectrolytes (plots of intrinsic viscosity verses polymer concentration in aqueous medium are concave upwards). This study paves the way for further investigation of solubility and viscosity behavior of this class of polymers.

# CHAPTER 5

# EXPERIMENTAL

## 5.1 Physical Methods

All m.p. are uncorrected. Elemental analyses were carried out in Carlo-Erba Elemental Analyzer Model 1102. I.R. spectra were recorded on a Perkin Elmer 16F PC FTIR spectrometer (Spectral resolution, 4 $cm^{-1}$; Number of scans, 19).

$^{1}H$ and $^{13}C$ NMR spectra of the polymers were measured in $D_2O$ using dioxane as internal standard and those of the monomers and precursors were measured in $CDCl_3$ using tetramethylsilane (TMS) as internal standard on a JEOL LA 500 MHz spectrometer. 5 mm diameter sample tubes were used at room tempeture. The $^{1}H$ observation frequency was 500 MHz and the spectra were obtained using a pulse width of 7.25 μs (45°) at a digital resolution of 0.31 Hz, sweep width of 10000.0 Hz and 16 scans. The $^{13}C$ observation frequency was 125 MHz and the spectra were obtained using a pulse width of 4.5 μs (20°) at a digital resolution of 2.01 Hz, sweep width of 33003.3 Hz and 10000 scans.

Viscosity measurements were made by Ubbelohde Viscometer (K 0.005989).

The equipment used for thermal analysis was a Simultaneous Thermal Analyzer (STA 429) manufactured by Netzsch, Germany. The polymer sample to be tested (usually 30 mg) was placed in one alumina crucible. The aluminum oxide ($Al_2O_3$, 100 mg), was placed in an identical alumina crucible as a reference sample. Using the sample carrier system, which has a pair of 10 percent Pt-Pt/Rh thermocouples, the sample carrier was placed in the middle of the vertical furnace, which was programmed and controlled by the microprocessor temperature controller. The temperature was raised to a uniform rate of 10 °C/min. The analyses were made over a temperature range of 20-1000 °C in a dynamic atmosphere of $N_2$ flowing at a rate of 100 ml/min.

## 5.2 Materials

Ammonium persulfate (APS) from BDH Chemical Co. (Poole, UK), t-butylhydroperoxide (80% in ditertiary-butylperoxide) and 6-amino hexanoic acid from Fluka Chemie AG (Buchs, Switzerland) were used as received. Methyl 6-aminohexanoate hydrochloride **(5)** was prepared as described.[69] All glassware were cleaned using deionized water. Dimethylsulfoxide (DMSO) was dried over calcium hydride overnight and then distilled under reduced pressure at b.p. 64-65°C (4 mm Hg).

## 5.3 Methyl 6-amino hexanoate hydrochloride (5)

A modified literature procedure[69] was used to convert 6-aminocaproic acid to methyl 6-amino hexanoate hydrochloride **(5)**. HCl gas (19.56g, 0.536mol) was absorbed in a solution of 6-aminocaproic acid (70.3 g, 0.536 mol) in methanol (108 mL) to yield a 0.86 N methanolic HCl solution. The absorption was carried out in a round-bottomed flask that was periodically weighed until the required weight of HCl was obtained. The solution was refluxed at 90 °C for 2 hour. Excess methanol was driven out by a stream of $N_2$ at 50 °C. The product was precipitated by adding ether (100 mL) and filtered using Buchner filtration. The residue was washed with ether (3 X 50 mL) while in the Buchner funnel, transferred to around bottomed flask and vacuumed at room temperature to constant weight. The product (95.0 g, 97.5%) is a white crystalline solid.

$\delta_H$(500 MHz, $CDCl_3$) 1.45(2H, m), 1.67(2H, quint, J 7.65 Hz), 1.81(2H, quint, J 7.50 Hz), 2.34(2H, t, J 7.35 Hz), 3.02(2H, broad s), 3.67(3H,s), 8.26(3H, broad s).

$\delta_C$ (125 MHz, $CDCl_3$) 24.16, 25.86, 27.20, 33.61, 39.71, 51.63, 173.92.(middle C 77.02, TMS 0.00).

## 5.4 Methyl 6-(*N*,*N*-diallyl amino)hexanoate (6)

Compound **(5)** (137.9 g, 0.7593 mol) was dissolved in methanol (450 mL) in a three-necked round-bottomed flask and 1/3 equivalent NaOH (30.37 g, 2.278 mol) was added. The mixture was magnetically stirred at 55°C for 1 hour while 1 equivalent allyl chloride was added dropwise over 20 min. Another 1/3 equivalent NaOH and 1 equivalent allyl

chloride was added in a similar manner and the mixture stirred for a further 4 hour at the same temperature. The resulting hydrochloride salt was neutralized with $K_2CO_3$ (52.47 g, 0.3797 mol) in water (75 mL) and the mixture was refluxed (66°C) 6 hour. Upon cooling two layers formed, the upper aqueous layer was decanted and extracted with ether (3 X 200 mL). The organic layer was combined with the ether extracts and dried with anhydrous $Na_2SO_4$. Ether was evaporated in a stream of dry $N_2$ at 50 °C. The product was chromatographed (activated $SiO_2$ column) with ether/hexane eluent (10-80% ether in hexane) to obtain the diallyl component. The product was distilled at reduce pressure through a 15 inch Vigreux distilling column (b.p $_{0.05\ mbar}$ 83°C). The product (102.3 g, 59.8%) is a colorless liquid.

$\delta_H$ ($CDCl_3$) 1.30 (2H. quint, J 7.6 Hz), 1.47 (2H, quint, J 7.6 Hz), 1.63 (2H, quint, J 7.6 Hz), 2.31 (2H, t, J 7.5 Hz), 2.41(2H. app. T, J 7.5 Hz) 3.07 (4H, d, J 6.6 Hz), 3.67 (3H, s), 5.14(4H, m), 5.84 (2H, m).

$\delta_C$ 24.89, 26.62, 27.02, 34.05, 51.48. 53.06, 56.86 (2C), 117.32 (2C), 135.79 (2C), 174.23. (middle C 77.02, TMS 0.00)

$\upsilon_{max}$. (neat) 3075, 2932, 2849, 2780, 1748, 1646, 1413, 1359, 1261, 1231, 1195, 1171, 1120, 999, and 921 $cm^{-1}$. M/z: 226($M^+$+1, 35.9%)

## 5.5 *N,N*-diallyl-*N*-carboethoxymethyl-*N*-carbomethoxy pentyl ammonium chloride (7)

A solution of (6) (20.28 g, 0.090 mol) and ethylchloroacetate (55.15 g, 0.45 mol) was stirred at 45°C for 72 hour. The reaction mixture was cooled and quaternary salt was

precipitated in ether (100 mL) forming two layers. The upper ether layer containing excess ethylchloroacetate was decanted off. The quaternary salt was partitioned with ether (6 X 50 mL) after dissolving in dichloromethane each time. After every partitioning the mixture was agitated to remove any remaining ethylchloroacetate. Finally the thick viscous liquid was dried under vacuum at 50 °C until constant weight (23.5 g, 75%).

$\upsilon_{max}$ (neat) 3371, 3080, 2946, 2868, 1741, 1469, 1434, 1371, 1213, 1171, 1106, 1022, 948, and 855 $cm^{-1}$.

$\delta_H$ ($CDCl_3$) 1.31 (3H, t, J 7.1 Hz), 1.42 (2H, quint, J 7.6 Hz), 1.96 (2H, app. quint, J 7.6 Hz), 2.35 (2H, t, J 7.1 Hz), 3.67 (3H, s and an overlapping 2H, m),4.25 (2H, q, J 7.1 Hz), 4.50( 4H, qd, J 7.4, 14.9 Hz), 4.67 (2H, s), 5.77 (4H, m), 6.12 (2H, m)

$\delta_C$ ($CDCl_3$) 13.93, 22.46, 24.13, 25.84, 33.55, 51.54, 56.81, 60.34, 62.72, 63.16 (2H), 124.60(2C), 129.64 (2C), 164.92, and 173.62 (middle C 77.53; TMS: 0.00).

## 5.6 Polymerization of (7) using ammonium persulfate (APS)

A solution containing 65% monomer by mass was prepared by adding the monomer (1.5 g) and dimethyl sulfoxide (1.65 g) in a 10 $cm^3$ round bottomed flask. Ammonium persulfate (APS) (5.4 g) was added and the closed flask was stirred at 40°C for 120 h. Viscosity of the mixture remained unchanged and there seemed to be no polymerization. The $^1H$ NMR spectrum confirmed that polymerization had not occurred. The reaction was repeated using 70% monomer solution in water and hydrogen peroxide (6 drops, 24 mg/g of monomer) was employed as initiator at 75°C for 72 h. However no polymerization product was obtained.

## 5.7 General procedure for the polymerization of (7) using tert-butyl hydroperoxide

A solution of monomer in deionized water (of appropriate concentration) was prepared in a 10 $cm^3$ round bottomed flask. The flask was purged with $N_2$ , closed and heated to 50°C. The flask was then briefly opened under $N_2$ to add initiator tert-butyl hydroperoxide. The mixture was stirred at 50°C for 24 h and then for a further 24 h at 75 °C. In one such experiment 83% w/w monomer solution and 10 mg initiator / g of monomer were used. The reaction mixture became noticeably viscous after the first 6 h and the magnetic stirrer stopped moving after 2 h at 75°C. The reaction mixture was cooled, transferred to a dialysis bag and dialyzed versus deionized water for 12 h. This was done to remove unreacted monomer. During dialysis the water surrounding the dialysis bag was tested with $AgNO_3$ for chloride ion (counterion on monomer) until all monomer had been removed. The pure polymer solution was then freeze dried and subsequently vacuum dried for 6 h at 70 °C until constant weight. Because of its hygroscopic nature the cream colored polymer was stored in dessicator. m.p. (Closed capillary) 134 –148 with color darkening above 214°C.

$\upsilon_{max}$. (neat) 3431, 2942, 2859, 1744, 1630, 1448, 1384, 1303, 1218, 1096, 1042, and 1019 $cm^{-1}$. (Found C:57.89, H:9.17, N:4.41. Calculated C:58.69, H:8.69, N:4.03.)

## 5.8 General procedure for copolymerization of the monomer (7) with $SO_2$ using ammonium persulfate (APS) initiator

The solvent dimethyl sulfoxide was dried over $CaH_2$ (24 hour) and distilled under reduced presure keeping the bath temperature around 70-80 °C. An appropriate amount of monomer was dissolved in DMSO and then a stream of $SO_2$ was passed over the solution until DMSO had absorbed the required mass of $SO_2$. In one experiment, monomer (10.4g, 0.030 mol) was dissolved in DMSO (5.8 g) and $SO_2$ (1.92 g, 0.030 mol) was absorbed in the monomer solution. The initiator ammonium persulfate was then added under $N_2$ and the closed flask was magnetically stirred at 50 °C for 20 h. The reaction mixture remained transparent throughout the polymerization process. The cooled reaction mixture was dialyzed versus deionized water (8 h) to remove unreacted monomer, $SO_2$, and solvent DMSO. A $AgNO_3$ test confirmed that monomer had been removed as described in section 5.5. The pure aqueous copolymer solution was freeze dried and then vacuumed at 50°C until constant weight. The hygroscopic white polymer was stored in dessicator.

m.p. (Closed capillary) 184 – 188 °C (decomposes turning yellow and chars at 237 °C)

$\upsilon_{max}$ (neat) 3439, 2942, 1738, 1442, 1312, 1220, 1169, 1126, and 1018 $cm^{-1}$.

(Found C:47.07, H:7.23, N:3.32. Calculated C:49.56, H:7.34, N:3.40.)

## 5.9 Acidic hydrolysis of the homopolymer (8)

A solution of homopolymer (10.0 g) was prepared in 6N HCl (200 mL) and stirred in a closed flask at 45°C for 120 h (until hydrolysis of the two ester groups was completed as

indicated by the absence of the methoxy and ethoxy proton signals from the 1H NMR spectrum). The reaction mixture was dialyzed against deionized water (to remove HCl). The aqueous polymer solution was basified with $NaHCO_3$ in the dialysis bag and dialysis continued to remove excess $NaHCO_3$ and NaCl (monitored by $AgNO_3$ test). The resulting solution was freeze dried and subsequently vacuum dried at 70°C until constant weight. The cream colored zwitterionic polymer was stored in a dessicator. Yield 8.29 g (99%).

$\upsilon_{max}$ (neat) 3429, 2942, 1630, 1570, 1404, 1328, and 723 $cm^{-1}$.

(Found: C:53.51, H:8.35, N:4.46. Calculated: C:57.72, H:7.61, N:4.81.)

## 5.10 Acidic hydrolysis of copolymer (10)

A solution of copolymer (10.0 g) in 6N HCl (200 mL) was stirred in a closed flask at 45 °C for 144 h (complete hydrolysis was confirmed by $^1H$ NMR). After about 2 h reaction time hydrolyzed copolymer started precipitating from solution. However at the end of the reaction the viscosity of the supernatant liquid suggested that some hydrolyzed polymer was in solution. Thus, the precipitated polymer and supernatant liquid were transferred to dialysis bag and dialyzed versus deionized water until all HCl was removed (monitored by $AgNO_3$ test). The aqueous polymer solution was basified with $NaHCO_3$ in the dialysis bag and dialysis continued until excess $NaHCO_3$ and NaCl was removed (checked by $AgNO_3$ test). The pure zwitterionic copolymer solution was freeze dried and then vacuum dried at 50°C for 6 h. The white copolymer was stored in dessicator. Yield 8.45 g (98%).m.p. (closed capillary): 227 - 232 °C (decomposes) and chars at 263 °C.

$\upsilon_{max}$. (neat): 3434, 2946, 1636, 1564. 1406, 1306, 1128, 910, 728, and 510 $cm^{-1}$.

(Found: C:44.94, H:6.85, N:3.74. Calculated C:47.31, H:6.24, N:3.94.)

## 5.11 3-(*N*,*N*-diallyl-*N*-methoxycarbonyl pentyl) ammoniopropane-sulfonate (13)

A solution of **(6)** (4.54g, 20.1mmol) and propane sultone (2.55g, 20.9mmol) in dry acetonitrile (70mL) was refluxed for 72 h. The solvent was evaporated in a stream of dry $N_2$ and the residue was purified by reprecipitation in ether (3X25mL). Yield 4.90 g (70%) of viscous liquid was obtained.

$\delta_H$ ($CDCl_3$) 1.38(2H, m),1.68(2H, quint, J 7.3 Hz), 1.85(2H, m), 2.27(2H, m), 2.34(2H, t, J 7.4 Hz), 2.86(2H, t, J 6.3 Hz), 3.17(2H, m), 3.64(3H, and an overlapping 2H, m), 3.99(2H, d, J 7.2 Hz), 5.73(4H, m), 6.03(2H ,sext, J 10.1 Hz)

$\delta_C$ ($CDCl_3$) 18.67, 21.39, 24.05, 25.63, 33.39, 47.22, 51.42, 57.70, 58.39, 60.67, 124.15, and 128.88 (middle C 77.00; TMS: 0.00)

## 5.12 Polymerization of (14) using t-butyl hydroperoxide

A solution containing 65% (w/w) monomer **(13)** was prepared by adding the monomer (1.96g) and water (1.06g) in a 10 $cm^3$ round bottomed flask. Initiator t-butyl hydroperoxide (27 mg) was added and the closed flask was stirred at 50°C for 24 h followed by a further 24 h at 75 to 80°C. The white polymer precipitated in the aqeuous reaction medium. The polymer was found to be insoluble in methanol and acetone. Unreacted monomer was removed by washing (6 times) the polymer with acetone. Pure dry polymer was obtained by vacuum drying at 60 °C for 6 h. Yield 93%. NMR sample was prepared by dissolving 80 mg polymer in 1.05g $D_2O$ containing 35.2 mg NaCl.

## 5.13 Solubility measurements

Solubility of polyelectrolytes **(8)** and **(10)** and zwitterionic polymers **(9)** and **(11)** in organic solvents at room temperature was determined for the 1% w/w polymer solution, after preheating at 70°C for 1 hour.

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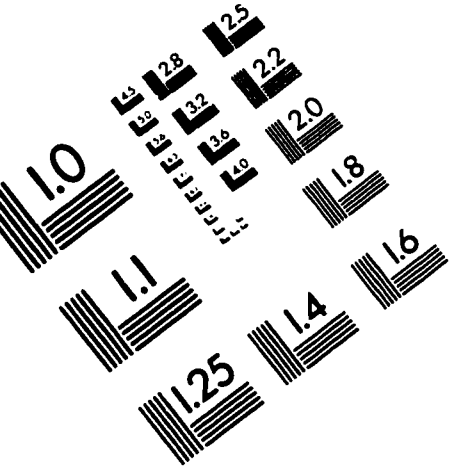


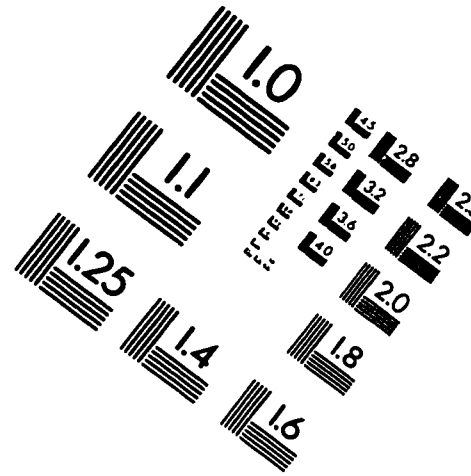


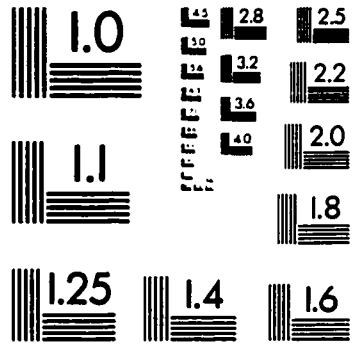


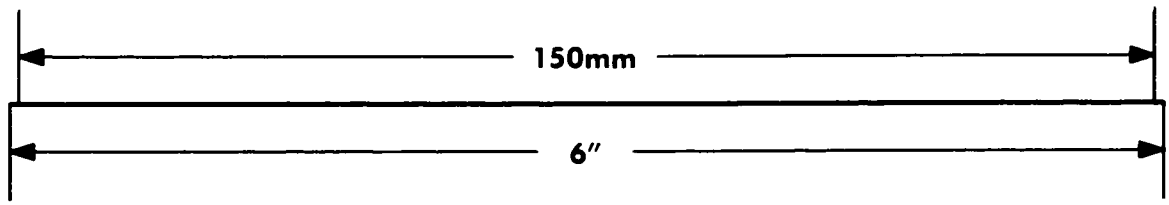


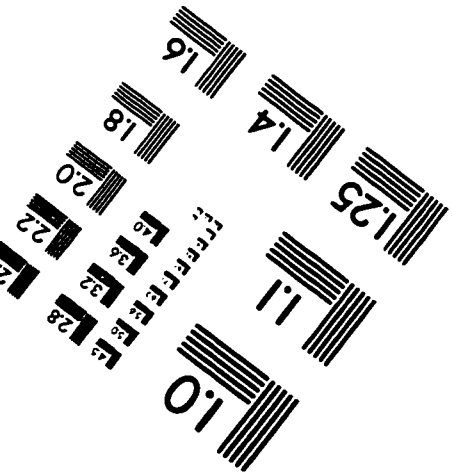


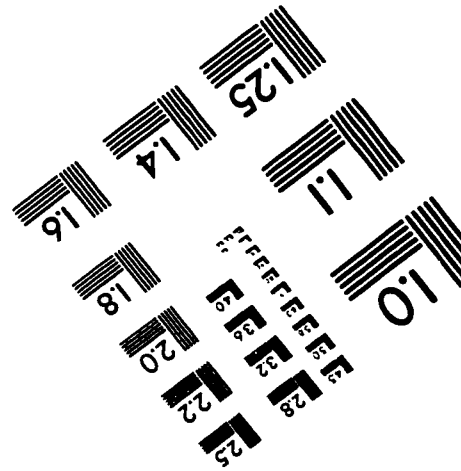


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